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**Federal Highway
Administration**

Guidelines for Handling Excavated Acid-Producing Materials

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FOREWORD

This study was funded as a part of the Coordinated Federal Lands Highway Technology Implementation Program. It is intended to serve the immediate needs of those who design and construct Federal Lands Highways, but is also made available to all other interested parties.

This study addresses the handling of acid-producing materials excavated in the process of road building. Guidelines for detecting and dealing with acidic drainage problems are developed for use during pre-design and construction phases of a project. Construction site variables such as topography, climate, hydrology and volume of material to be excavated necessitate site-specific planning. Embankments designed for encapsulating acid-producing material are recommended based upon testing performed during this study.

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16. Abstract Earth materials containing greater than 0.5% by weight pyritic sulphur and having little or no alkaline content when exposed during construction can adversely impact the environment through the production of acidic drainage (AD). Chemical weathering, accelerated by the greater surface area created by excavation, generates acid which in-turn mobilizes metals that are potentially toxic to aquatic biota. This study addresses handling of acid-producing materials excavated in the process of road building. Guidelines for detecting potential AD problems and for dealing with the AD problem, generated through literature review, case studies, and research, are organized for use during the pre-design, and construction phases of a project. Due to the diversity among construction sites, there can be no generic plan for coping with the potential AD problem. Site variables, including, topography, volume of material to be excavated, climate, and hydrology, necessitate site-specific planning. Embankments designed for encapsulating acid-producing material are recommended based upon testing performed during this study. All rock to be exposed through excavation should be considered suspect for AD production until proven otherwise through geologic and/or geophysical investigations.			
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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
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LENGTH

in	inches	25.4	millimetres	mm
ft	feet	0.305	metres	m
yd	yards	0.914	metres	m
mi	miles	1.61	kilometres	km

AREA

in ²	square inches	645.2	millimetres squared	mm ²
ft ²	square feet	0.093	metres squared	m ²
yd ²	square yards	0.836	metres squared	m ²
ac	acres	0.405	hectares	ha
mi ²	square miles	2.59	kilometres squared	km ²

VOLUME

fl oz	fluid ounces	29.57	millilitres	mL
gal	gallons	3.785	litres	L
ft ³	cubic feet	0.028	metres cubed	m ³
yd ³	cubic yards	0.765	metres cubed	m ³

NOTE: Volumes greater than 1000 L shall be shown in m³.

MASS

oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams	Mg

TEMPERATURE (exact)

°F	Fahrenheit temperature	5(F-32)/9	Celcius temperature	°C
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APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
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LENGTH

mm	millimetres	0.039	inches	in
m	metres	3.28	feet	ft
m	metres	1.09	yards	yd
km	kilometres	0.621	miles	mi

AREA

mm ²	millimetres squared	0.0016	square inches	in ²
m ²	metres squared	10.764	square feet	ft ²
ha	hectares	2.47	acres	ac
km ²	kilometres squared	0.386	square miles	mi ²

VOLUME

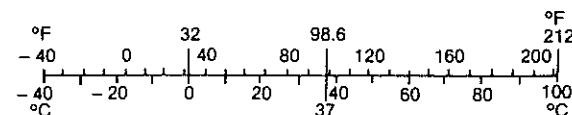
mL	millilitres	0.034	fluid ounces	fl oz
L	litres	0.264	gallons	gal
m ³	metres cubed	35.315	cubic feet	ft ³
m ³	metres cubed	1.308	cubic yards	yd ³

MASS

g	grams	0.035	ounces	oz
kg	kilograms	2.205	pounds	lb
Mg	megagrams	1.102	short tons (2000 lb)	T

TEMPERATURE (exact)

°C	Celcius temperature	1.8C + 32	Fahrenheit temperature	°F
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* SI is the symbol for the International System of Measurement

(Revised April 1989)

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INTRODUCTION

Acid-producing material is herein defined as any earth material capable of producing acidic drainage (AD) upon weathering, where AD is considered to be water having pH values of 4.5 or less, and weathering is a natural process in which earth materials are chemically/biologically decomposed and/or physically disintegrated. Excavation during construction facilitates weathering and the potential for AD by increasing the surface area of fresh rock for chemical reactions. The material most commonly prone to produce AD is rock containing pyritic sulfur in excess of 0.5 percent and containing little or no alkaline minerals. AD adversely impacts the environment, especially aquatic systems; therefore, the potential for AD must be given serious consideration during any project involving the disturbance of earth material. When significant amounts of acid-producing materials are detected, provisions for special material handling are necessary.

Special handling of acid-producing material increases the cost of a construction project well above the normally anticipated cost for construction in a given area. However, the additional costs are significantly lower when the potential problem is addressed and handled prior to and during construction than the additional costs for mitigation of any adverse environmental impacts following construction.

The purpose of this document is to present guidelines for handling acid-producing materials during road construction. These guidelines have been generated through literature review, case studies, participation in seminars and workshops dealing with similar AD problems, and the evaluations of laboratory and field tests conducted by the principle investigator. Research addressing the problem of AD is an on-going process by many investigators, thus the guidelines presented here can only express the state of the art as it exists at this moment. The tests and analyses suggested in these guidelines, being based upon the current technology, are judged to be the best. The suggested handling strategies are based upon results cited in the literature, but mainly upon the evaluation of laboratory and field experiments, as well as current practices used in the field. Hopefully, efforts will continue through time to improve the methods and strategies presented here.

For the convenience of application, the guidelines are presented in three sets with each set being concerned with a different stage in the construction of a road project. The first two sets of guidelines are for the planning phases of a project and the last set is to be considered during the construction phase of a project. The first set of guidelines concerns the pre-design stage of a project which normally embraces the time span during corridor selection, the second set of guidelines is applicable to the design phase of a

project, and the last set of guidelines pertains to actual handling acid-producing material during project construction. Each set of guidelines should be used in succession and predicated upon the data derived from the guidelines for the preceding phase of the project. In other words, project design should be based upon data derived from pre-design investigations, and handling of the acid-producing materials during construction should follow guidelines of the best strategy as determined in the guidelines of the design phase. Thus, the guidelines are to be used as the means by which a potential problem can be identified, a means to define the extent of a problem, and a means to devise the best strategy to handle the problem.

A strategy selected for handling acid-producing material must be site specific. No two construction situations are likely to be identical, thus there can be no generic plan that covers all construction situations. The site variables that necessitate site specific planning include: topography, volumes and types of material (rock and soil) to be excavated and handled (good quality : sulfidic), climate, and hydrology.

GUIDELINES FOR PRE-DESIGN PHASE OF PROJECT

Pyrite and related sulfide minerals are ubiquitous in the materials of the Earth's crust, albeit certain rock types tend to have higher

average concentrations than others. Pyrite, a mineral that forms in high temperature as well as low temperature geologic environments, is associated with all three classes of rocks - igneous, sedimentary, and metamorphic. Pyrite may sometimes be considered as a primary ore, but more commonly it is part of the gangue (uneconomical) minerals occurring with the primary ore mineral(s) in a deposit. The principal product derived from mined pyrite is sulfuric acid.

Aside from the anomalous concentrations of sulfides in earth materials constituting ore deposits, the most problematic occurrence of the iron-disulfide minerals is within sedimentary rocks or metasedimentary (metamorphic sedimentary rocks) rocks having mineral assemblages with little or no capacity for producing alkalinity. These are most commonly carbonaceous (high carbon content) shales or argillaceous rocks. The sulfidic nature of these rocks can generally be attributed to the enoxic (reducing) conditions of the ancient environments in which the sediment accumulated. Coal is sulfidic for this reason. The pyrite (or more commonly the polymorph, marcasite) is often finely disseminated within these rocks, and of a form that easily disintegrates, making it very accessible to the reactions resulting in acid generation.

Coarser textured sedimentary rocks, low in alkaline-producing mineral content, like sandstone, may also contain appreciable amounts of sulfide minerals capable of producing AD,

especially when they are associated with sulfidic argillaceous rocks. A common fallacy is that only dark colored rocks have the propensity to generate AD; however, many light-colored rocks such as most sandstone and siltstone when not duly considered as potentially deleterious, have, to the surprise of some, produced AD.

The most important point to be made is that all rock materials should be considered suspect and reference should be made to available geologic literature pertinent to the composition of the rocks in the area under consideration. Such an investment of time and resources can serve as an alert to any potential problems and permit development of plans for thorough site specific exploration.

The topographic setting of a project has a strong bearing on development of a strategy for handling encountered acid-producing materials. Steep and rugged topography probably presents the worst of the possible situations. Large volumes of material are usually involved in constructing the excavations and embankments required for maintaining the prescribed grade in mountainous terrains. An additional problem in such a setting is the availability of borrow material, especially if a large volume is needed to encapsulate pyritic rocks. The logistics of handling acid-producing materials under such conditions probably presents a greater impact on the economics of construction than it does in

any other setting.

Water and temperature are the important factors in chemical weathering; therefore, the climatic conditions of a proposed project location must be given due consideration. Although moisture is to be considered the more important factor, acid-producing material in the presence of a warm and humid climate is more susceptible to AD than it is in a cool and dry climate. The surface drainage of a construction site as well as the subsurface water regime should be considered in any strategy for handling the acid-producing material. Figure 1 illustrates the influence of climate upon the chemical weathering process.

The guidelines suggested below are for the cursory evaluation of material along a proposed road corridor, and they are applicable to both new construction and improvements to existing roads. Any case where excavation of material and the construction of new embankments are considered, should be explored for the presence of acid-producing material.

The first step in the guidelines is to consult all available geologic information pertinent to the project area. This includes reviewing all published geologic maps and literature and consulting with geologists familiar with the area. If no literature or maps are available, or if other geologic information consulted indicates the probable presence of acid-producing material, the following steps should be followed:

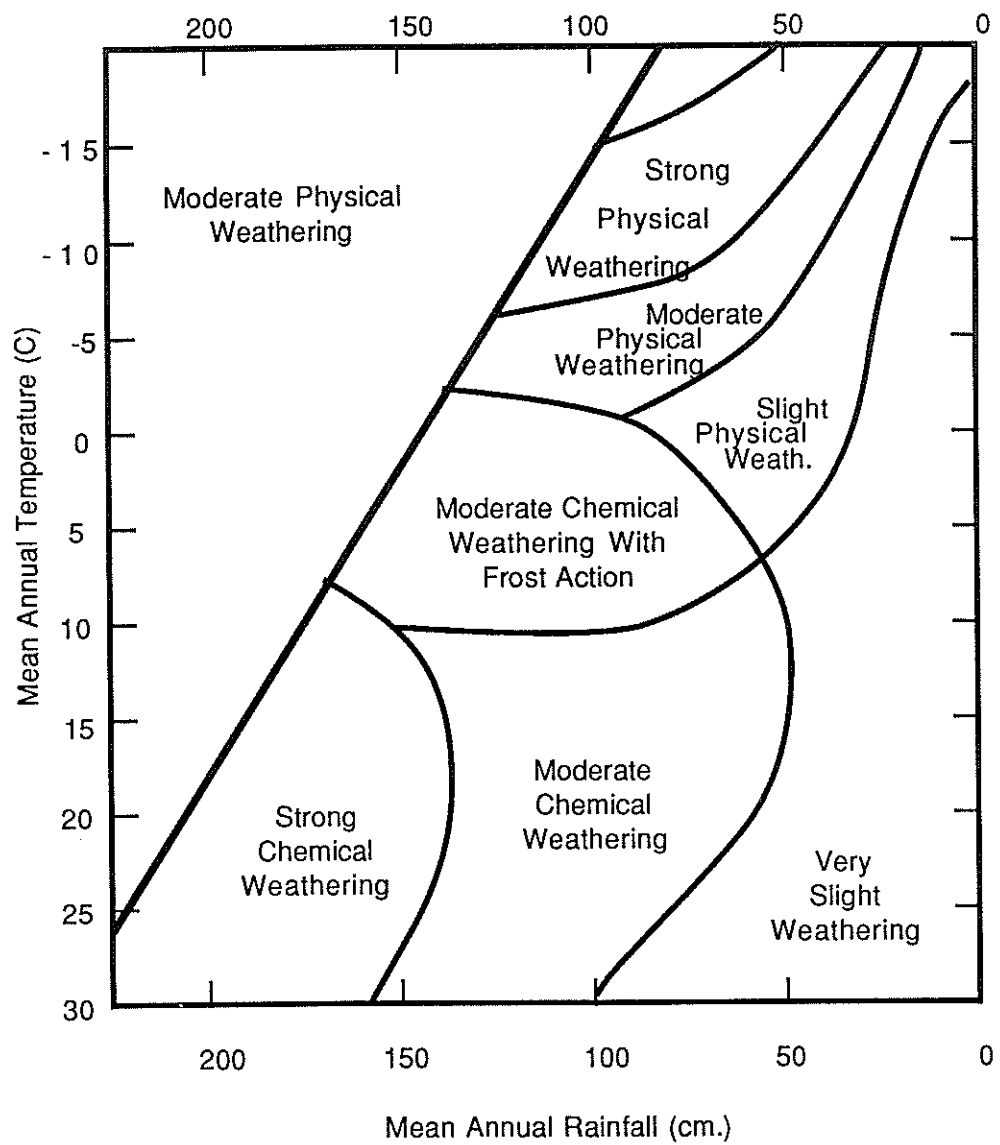


Figure 1. Climatic influence upon chemical weathering. (1)

- Map and sample outcrops along the corridor.
- Sample all rock core produced by exploratory drilling.
- Analyze rock samples for Net Neutralization Potential (NNP) using the Acid-Base Accounting procedure.
- Conduct geophysical investigations such as Induced Polarization or Self-Potential (IP or SP) surveys.
- Establish a water quality monitoring plan in the event that acid-producing material is identified.

Geologic Mapping and Sampling

Using geologic maps assumes that detailed ones are available for the area or that there are adequate outcrops (bedrock exposures) along the proposed corridor to permit detailed mapping and sampling. Sources of published geologic maps and other data useful for site evaluation include: State geological surveys, the United States Geological Survey, college and university geology departments, and mining companies.

The detail and quality of geologic maps vary considerably. To be useful as a tool for evaluating the character of the rocks in an area, maps should be constructed on a scale of 1:24,000 or larger and be accompanied by a

report with mineralogic descriptions of all the rock units embraced by the mapped area. When the presence of sulfidic rocks is indicated by existing maps, regardless of how detailed the existing maps may be, site specific mapping and sampling along the corridor must be done. Besides specifically evaluating those rocks exposed, geologic mapping of the corridor can locate data gaps where bedrock is not exposed. If the bedrock in the intervals where rock is poorly exposed is considered to be a potential acid-producer on the basis of other geologic data sources, then further exploration of these gaps can be more efficiently planned utilizing other techniques.

Sometimes an assessment of the potential for AD can be made even though maps and other information may not be available for the immediate project area. This can be done by noting the proximity of the proposed project to known active or abandoned mining sites (coal, uranium, metals, etc.) or construction projects that may have experienced AD problems, and then extrapolating this information.

Borehole Sampling

All rock core from exploratory drilling should be carefully examined for its mineral content as well as its physical character. There are, however, limitations to the amount of information that can be derived from the study of borehole logs. In most instances exploratory boreholes are spaced along a proposed corridor mainly

where major cut slopes are anticipated in order to provide information on soil depth and rock character. Due to this spacing little or no knowledge may be obtained about the mineralogic character of the bedrock in what may be very large gaps between boreholes, and although major cuts may not be planned for these intervals, bedrock may be excavated in these intervals for such purposes as benching for a fill slope.

In some cases, samples can be collected from the cuttings of air drills. This type of drilling is less expensive than core drilling and can provide composite samples for various depth intervals that are suitable for acid-base accounting analyses. This type of sampling is best suited to rock quality control during construction when sampling can be performed on future exposures by sampling blast holes.

Rock Sample Analyses

The presence of pyrite and other sulfidic minerals can ordinarily be detected megascopically. However, because the sulfide minerals can be very minute and nearly invisible, certain rocks such as dark, carbonaceous rocks should routinely be suspected of having a sulfide mineral content. When a rock is visually estimated to contain an approximate sulfide mineral content of 1 percent or more per volume it should be analyzed to determine its acid potential. Many different tests have been used to evaluate the relation-

ship between AD potential and the sulfide minerals present, but the test selected as most appropriate for these guidelines is the Acid-Base Accounting procedure.(2) Among reasons for selecting this test are that: it produces reasonably rapid results, the correlation between the predicted values and the real-world values is acceptable for predicting potential worst case conditions, and the analysis is relatively inexpensive. Table 1 is an example of typical data generated by acid-base accounting tests of samples collected from a highway project.

In this test representative samples of the rock to be excavated are collected and prepared for analysis. A small portion (<1g.) of the pulverized sample is combusted in a furnace liberating SO_2 which is measured in %S. The amount of Acid Potential (AP) in tons CaCO_3 per 1,000 tons of material is derived stoichiometrically from the %S. A Neutralization Potential (NP) is determined by hot acid digestion (HCl) of pulverized sample and then titration with NaOH. The NP is also expressed in terms of tons CaCO_3 per 1,000 tons of material. The Net Neutralization Potential (NNP) is the NP excess or deficiency determined by subtracting the AP from the NP. An NNP value of - 5 tons CaCO_3 or less is generally interpreted as predicting potential AD (2).

However, consideration must be given to the volume of material having low NNP relative to the total volume excavated in order to make

a sound decision as to what may constitute a potential AD problem. In some cases a large volume having NNP values of -5 or less should be totally encapsulated; whereas, small quantities of material having NNP values between -5 and -15 can be blended and used

with precaution as common fill.

For the examples depicted in table 1 no volumes of excavated material are indicated. However, for the material to be excavated between stations 350+00 and 355+50, it can be generalized that low NNP values represent

Table 1. Examples of acid-base accounting data.

Sample Sta.	Lithology	Visual Pyrite > 1%	%S	AP	NP tons CaCO ₃ /1000 tons	NNP
350+00	Arg.	Yes	0.4	13.8	6.6	- 7.2
350+50	Slt.	Yes	1.3	40.6	12.2	- 28.4
351+50	Ss.	Yes	3.2	99.9	8.0	- 91.9
352+00	Ss.	Yes	0.0	0.0	8.5	+ 8.5
353+00	Ss.	Yes	0.2	7.2	15.9	+ 8.1
354+00	Ss.	Yes	0.5	16.7	8.5	- 8.1
354+40	Ss./Arg.	Yes	3.2	100.3	10.2	- 90.1
355+00	Arg.	Yes	0.2	7.7	2.9	- 4.8
355+50	Ss./Arg.	Yes	3.4	107.7	3.9	-103.8
058+50	Arg.	No	0.0	0.0	2.5	+ 2.5
059+00	Arg.	No	0.0	0.0	1.7	+ 1.7
059+35	Arg.	No.	0.0	0.0	1.5	+ 1.5
059+50	Arg.	No	0.4	13.4	2.2	- 11.2
060+00	Arg.	No	0.0	0.0	1.7	+ 1.7
060+50	Ss./Arg.	No	1.2	36.2	21.6	- 14.6
060+75	Arg.	No	0.01	1.2	1.2	0.0

AP = Acid Potential; NP = Neutralization Potential; NNP = Net Neutralization Potential; Ss. = Sandstone; Arg. = Argillite; Slt. = Siltstone

the bulk of the material and that special handling should be required to avoid AD. Material at two stations within that interval (353+00 and

354+00) have moderately low NNP values when compared to the high NNP deficiencies at the other stations, but unless these

materials can be readily separated from the total excavated volume (a judgement made in the field), they should be treated as a part of the total excavation (350+00 to 355+50) and appropriately encapsulated as acid-producing material.

On the other hand, the NNP values for samples of material between stations 058+50 and 060+75 are preponderantly positive, and if the volume of material at stations 059+50 and 060+50 is not substantial (field determination), blending of the material with the total excavated volume of the interval may render it usable as common fill.

Geophysical Tests

Resistivity, or the inverse of the ability to conduct an electrical current, is the main basis of the geophysical methods used to predict the presence of sulfide minerals in the sub-surface. Two methods that have had some degree of success in detecting the presence of pyritic rock along proposed highway corridors are Induced Polarization (IP) and Self-Potential (SP).(3,4)

In the case of a dipole-dipole IP survey along the corridor of a proposed highway, the derived data are generally expressed as Metal Factor (MF), Percent Frequency Effects (PFE), and Resistivity (R). The PFE values indicate polarizable areas without regard to the resistivity (R) of an area. The MF is obtained by combining the PFE and the R values. Good

conductors (low resistivity) that are strongly polarizable (high PFE) present well defined or "definite" MF anomalies. Less well defined MF anomalies are designated as probable or possible mineralized areas. The PFE and MF parameters are complementary.(3)

- PFE responses greater than 10 percent are considered indicative of high concentrations of sulfides or other polarizable materials.
- R values less than 10,000 ohm meters indicate the presence of rocks easily weathered (presence of interstitial space and/or water).
- MF values (derived from the combined PFE and R values) greater than 1 indicate easily weathered sulfidic material.

IP data with R values greater than 10,000 ohm meters and PFE values less than 2 percent are interpreted as dense and compact rock with structural characteristics from which sulfides, if present and in an undisturbed state, would not likely be oxidized. Very resistant rock ($R > 10,000$ ohm meters) with very low metal factors ($MF < 1$) generally correspond to rock with low sulfur ($< 1\%$); however, in some instances rock with high MF values have been found to actually have low S%. Other constituents in the rock that are good conductors, but low in sulfur content, such as graphite, can give such misleading

data. Also, it should be noted that IP data cannot predict the presences or absence of minerals capable of providing a buffering capacity to the chemical environment. Table 2 clearly indicates that there is not always a clear correlation between the predictions of the

geophysical data of an IP survey and those of the chemical data from the acid-base accounting analyses.

The samples in table 2 are arranged in sequence from highest MF value to lowest MF value. It is notable that samples 7,10, and 12,

Table 2. Comparison of IP and acid-base accounting data.

Sample	Lithology	R	IP DATA		ACID-BASE ACCT.	
			PFE	MF	%S	NNP
1	Ss.	442	21.0	47.0	1.42	-33.4
2	Arg.	442	21.0	47.0	2.31	-67.9
3	Arg.	435	18.0	41.0	1.02	-24.4
4	Ss.	215	6.9	32.0	1.59	-43.2
5	Arg.	832	16.0	19.0	0.51	-12.4
6	Arg.	1,187	17.0	14.0	0.88	-21.2
7	Ss.	2,090	10.0	4.8	0.10	+17.9
8	Arg.	1,860	8.5	4.6	1.72	-50.0
9	Ss.	2,690	12.0	4.3	0.51	-11.1
10	Arg.	4,600	11.0	2.4	0.05	+ 6.9
11	Ss.	4,160	8.4	2.0	1.40	-35.3
12	Arg.	7,225	13.0	1.8	0.05	+ 5.7
13	Arg.	4,530	6.4	1.4	0.18	- 2.3
14	Slt.	6,890	9.2	1.3	0.96	-27.5
15	Slt.	8,260	9.4	1.1	1.67	-49.4
16	Ss.	7,340	4.8	0.7	0.00	+ 3.5
17	Ss.	6,879	2.7	0.4	0.04	+ 2.7
18	Ss.	22,550	3.4	0.2	0.00	+13.3

Ss.= Sandstone

Arg.= Argillite

Slt.= Siltstone

although having MF values higher than 1, have positive NNP values. This is a case, perhaps

where the IP data fail to indicate the presence of materials with a buffering capacity, or

possibly that the high PFE values may indicate the presence of metallics other than sulfide minerals. The latter interpretation may be more feasible based upon the fact that samples 7, 10, and 12 all have low percentage sulfur values. Samples 7 and 8 have very similar IP data, yet sample 8 with a slightly lower PFE value which should indicate less sulfide mineralization, has a very high acid potential according to the acid-base accounting data.

Induced Polarization surveys, regardless of the dipole spacing are time consuming and labor intensive. Typically in rugged terrain it requires a 3 to 5 member crew a day to survey up to 3,000 ft (900m).

Self-Potential (SP) surveying should be considered as a viable alternative to IP for reconnaissance surveys, especially in rugged terrain. The SP method is more rapid and can be accomplished by a two-person crew. The SP survey is based upon the interaction between the natural oxidation-reduction potential gradient in the earth and electronically conductive minerals such as pyrite.(4)

The oxidation-reduction potential gradient causes an electronic current to flow in the mineral grains, and voltages called self-potentials are generated by the return current flow through ionically conductive pore fluids in the soil and rock surrounding the mineral deposit. Because near-surface pore waters are more oxidizing than those at depth, the return current above a mineral deposit flows downward and generates a negative SP

anomaly (relative to background values). SP anomaly amplitudes are expressed in millivolts (mV). One mV equals 1/1000th of a volt. A comparison of IP and SP data with AP test results can be seen in appendix B.

Geophysical surveying should be considered as a tool to predict the presence of acid-producing materials in two situations. First, when pyrite presence is indicated by means of geologic literature or by means of cursory inspection of rock specimens (from outcrops or core), but rock is poorly exposed through a proposed corridor. The use of IP or SP in this situation is likely to be more economical than closely spaced boreholes; plus the geophysical survey will give continuous data on those intervals that would ordinarily be gaps between boreholes. Dipole spacing of approximately 200 ft (60 m.) is used for reconnaissance surveying with IP, while a closer dipole spacing may be required for higher resolution of the occurrence of the sulfidic mineralization. Secondly, geophysical surveying should be considered as a tool to provide data for corridor distances between rock outcrops and/or boreholes where data from these sources are available.

Summary

Although prediction is considered to take place before the fact, it is important that predictive procedures be followed throughout all phases of road construction. Predictive meas-

ures should be taken along a proposed road corridor in advance of any design developments and continue throughout all subsequent phases until a project is completed.

Figure 2 is a flow chart that provides a general outline of steps that can be followed during the pre-design phase of a project:

1. A corridor is proposed.

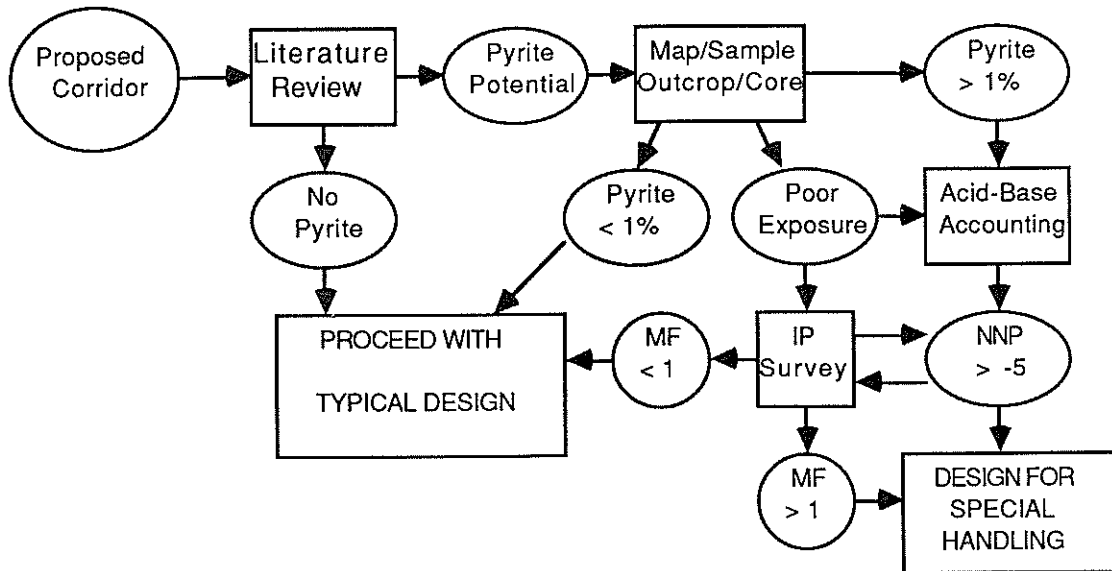


Figure 2. Flow chart of steps in pre-design guidelines.

2. The geology of the corridor is evaluated for the potential occurrence of acid-producing material using literature or the extrapolation of information from nearby sites.

A. Pyrite presence is not indicated.

(1) Proceed with road design.

B. Pyrite occurrence is highly probable.

(1) Proceed to guideline 3.

3. Thoroughly examine by geologic mapping and sampling (available core should be

examined) the bedrock within the corridor.

A. Representative samples cannot be examined due to extensive soil cover.

(1) Proceed to guideline 5.

B. Pyrite content is low; where detected it constitutes less than 1 percent of the rock volume.

(1) Proceed with road design, but continue to monitor all rock exposed by boreholes, etc.

C. Pyrite is pervasive and constitutes more than 1 percent of the volume of the examined rocks.

- (1) Test rocks using acid-base accounting procedure.

4. Review acid-base accounting test results.

A. If all sampled rocks have excessive NP values ($NNP > -5$):

- (1) Proceed with road design, but continue to monitor all rocks exposed by boreholes etc.

B. If any sampled rocks have deficient NP values ($NNP < -5$):

- (1) Consider design for special handling.
- (2) Consider geophysical surveying for all or parts of the corridor.

5. Geophysical surveying.

A. $MF > 1$ corroborating acid-base accounting data:

- (1) Design for special handling.

B. $MF < 1$ with no indication of sulfide minerals:

- (1) If other data (acid-base accounting and/or visual inspection) suggest presence of acid-producing material, continue with guideline 3C.

GUIDELINES FOR DESIGN PHASE OF PROJECT

It is assumed that at this point the major zones of acid-producing material have been delineated. Geologic structural data should be consulted, if it has not already been compiled during geologic mapping, in order to ascertain the geometry of the materials considered to be acid-producing. The use of these data may permit major changes in the design, such as shifting of the corridor alignment or adjusting the grade to avoid or minimize excavation of the acid-producing material. Judgements of this nature are best accomplished during "plan-in-hand" reconnaissance of the corridor line.

The strategy at this point is largely dependent upon how much preliminary design work has been done. If some design work has already been done, estimated volumes of non-acid-producing and acid-producing material can be calculated from constructed sections. If not, volume estimates can be made from existing topographic maps. In all cases provisions must be made in the project design for encapsulating the material judged to be acid-producing ($NNP < -5$; $MF > 1$), either on the project as part of the embankment design or at a nearby environmentally acceptable site.

As previously pointed out, the handling of acid-producing material on each project must be considered as a specific case. Each project can offer an almost unlimited combination of

conditions that can be encountered. These conditions involve such variables as the relative volumes of good and potentially deleterious material, topography, structural geology, bedrock geology, climate, and hydrology. Rigid guidelines cannot address all of the possibilities and therefore would not be applicable in all situations. The guidelines presented here are flexible enough to take into consideration variations in conditions where acid-producing materials are most likely to be encountered.

Table 3 is a chart that shows some of the possible combinations of conditions that must be considered during the design phase of a project. On this chart topography is generalized into three categories: steep, which suggests mountainous terrain; moderate, suggesting rolling hills with moderate relief; and flat, which suggests relatively level ground. Two typical rock relationships are represented on the chart. One for coal-related strata and one for metasedimentary rocks such as occur in the southern Appalachian Mountains, an area where acid-producing materials are known to pose problems. Each rock type category is further subdivided into categories of those rocks having some carbonate rock in the association and those not having carbonate rocks in the sequence. The geologic structure is either that of relatively flat-lying strata or rocks that have been tilted and contorted through folding and/or faulting. Location of encapsulation refers to whether

the material must be used in the balancing of excavated volumes on the project or whether the acid-producing material can be transported off site to an environmentally safe encapsulating site.

Where acid-producing rocks are to be handled the following points should be considered during the design phase:

- Excavation of the acid-producing rock should be avoided where possible and always minimized.
- Sites for disposal of all anticipated acid-producing rock should be identified.
- Borrow sites from which adequate quantities of cover material for burial of the sulfidic rock should be identified.
- Logistics for hauling acid-producing material, the lime and limestone, and cover material to the disposal sites during construction should be determined so as to eliminate, if possible, temporary storage of the acid-producing rock.
- Drainage should be diverted away from all excavations and encapsulating embankments.
- Ditches and other waterways along excavated and encapsulated acid-producing

Table 3. Factors controlling design for handling acid-producing material.

% Excavated Volume Pyritic	Topography			Climate		Rock Types				Geologic		Location of
	Steep	Mod.	Flat	Humid	Dry	Coal Related		Metasediment.		Structure		Encapsulation
						Carb	No Carb	Carb	No Carb	Hor.	Deform	
1 - 33%												On Site
												Off Site
34 - 66%												On Site
												Off Site
67 - 100%												On Site
												Off Site

material should be asphaltic or concrete paved.

- Underdrains, pipe culverts, and storm drains in areas of excavated and encapsulated acid-producing material should be constructed of concrete or inert plastic.
- Encapsulation of pyritic material should follow an acceptable design, either on site or off site.

Encapsulation of acid-producing material in some instances can be avoided or at least minimized by shifting the corridor alignment or by modifying the grade. This is more likely to be possible when the rocks to be excavated occur in inclined or deformed layers. Figure 3 illustrates one possibility of shifting a line outward to minimize the amount of material to be excavated from an inclined layer of sulfidic rock.

Table 4 is a comparison of quantities and cost estimates (1987 dollars) calculated for handling acid-producing materials on a project in mountainous terrain. This scenario presents two lessons. One, that it is economically prudent to consider more than one option for material handling, and secondly, that it is very important to carry out a thorough pre-design evaluation of material. In this particular case none of the options were tenable, due to the

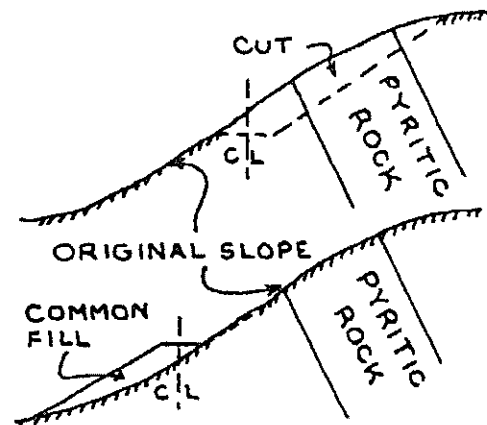


Figure 3. An example of alignment shifting to minimize excavating pyritic material.

fact that an insufficient quantity of borrow material was available to satisfactorily encapsulate the pyritic rock. In this particular case these options were evaluated when an unpredicted 19,619 yd³ (15,000 m³) of pyritic rock were encountered near the terminus of a project. In this situation the encapsulating design being used would have required an embankment capacity of 32,694 yd³ (25,000 m³); however, the planned alignment would only accommodate 2,251 yd³ (1,721 m³). The total costs presented in table 4 reflect costs for excavation and handling the pyritic rock over and above the costs of the original contract.

Cut slopes in acid-producing rock should be as near vertical as the rock structures will allow. This reduces the area of the rock face that

Table 4. Earthwork comparison example.

	Original Line	Line Shift/Grade Change	Line Shift	Grade Change
Excavation:				
Quantity	27,155	5,078	8,710	9,462
Cost	\$65,173	\$12,186	\$20,903	\$22,709
Borrow:				
Quantity	-735	93,161	41,343	48,235
Cost	\$0	\$223,586	\$99,224	\$115,536
Pyrite Embankment:				
Quantity	32,699	20	4,633	5,768
Cost	\$65,397	\$40	\$9,266	\$11,536
Lime:				
Quantity	121	0.1	17.2	21
Cost	\$12,139	\$7	\$1,720	\$2,141
Ls. Blanket:				
Quantity	2,207	1	313	389
Cost	\$51,316	\$3	\$7,271	\$9,052
TOTAL COST	\$194,025	\$235,025	\$138,384	\$161,202

would be exposed to weathering; permitting faster runoff and less infiltration of precipitation. Pyritic bedrock that necessitate cut slopes of 1.5:1 or flatter should be hydro-seeded and mulched.

The location of a burial site directly on the project or at an acceptable location off site must be considered during design. Acid-producing material cannot be handled in a "the material can be handled as it is encountered" fashion. All anticipated quantities of acid-producing material must have a designated site for disposal. It may also be prudent to have a contingency plan in the design to handle small quantities of acid-producing material that may be encountered, but were not delineated by pre-design testing.

On site burial is perhaps the most practical method for handling pyritic material; however, if the estimated volume to be excavated on a project contains excessive quantities of good quality rock that must otherwise be wasted, one or two environmentally acceptable sites within economically reasonable haul distance can be selected for all burial. However, regardless where the burial is sited, design must consider the following:

- The quantity of acid-producing material that can be placed.
- The quantity of lime, limestone, and cover material that will be required to construct the special embankment.

- The hydrology of the proposed site.

It is best, when possible to encapsulate acid-producing material in several large, well-constructed embankments, than to spread the material in many smaller embankments throughout the project. The rationale for this strategy is that remedial treatment would be facilitated, if later found necessary.

The ratio of the quantity of acid-producing material to be encapsulated to the amount of cover material determines the design strategy to be used for an encapsulating embankment. On projects where the over all balancing of volumes of material is affected by large quantities of acid-producing material, minimal design criteria can be used; however, under no circumstances should the integrity of an encapsulation be compromised.

Whatever handling technique is used for encapsulating acid-producing material, it must address the factors responsible for generating AD. These factors include:

- Primary Factors:

1. Iron-disulfide minerals.
2. Oxygen.
3. Water.
4. Acidophyllic bacteria.

- Secondary Factors:

1. Alkalinity-producing materials.
2. Ionic exchange capabilities of materials.

- Tertiary Factors:

1. Site drainage.
2. Grade and compaction of materials.
3. Vegetation.

Any preventive or abatement strategy considered viable for a particular site must accomplish one or more objectives aimed at controlling the factors responsible for the generation of AD. In other words, any adopted design for encapsulation must address one or more of the the following purposes:

- Control oxygen.
- Control water.
- Enhance alkalinity.
- Control bacteria.
- Remove sulfides.

Oxygen reduction is accomplished in encapsulation by three means:

1. Burial of acid-producing material as soon as possible after being exposed by excavation.
2. All embankment material must be compacted throughout construction of the burial site, especially during placement of the pyritic rock. This reduces the voids between the rock fragments.
3. Surface and outslope material must be compacted in order to decrease oxygen diffusion into the embankment.

Figure 4 is a model that illustrates four zones in a typical backfill which contain different concentrations of oxygen.(5) In figure 4 zone I is located within 5 ft (1.5 m) of the surface and is the most highly oxidized area of the embankment. Zone II is the encapsulated material where air and water are minimized. Zone III is an area of non-toxic material, and zone IV constitutes the bench and possibly a saturated area. The investigators observed that zone I does not prevent oxygen diffusion into zone II, but oxygen concentrations are reduced 3 to 6 ft (1 to 2 m) down from the surface.

Because affected water constitutes AD, great care should be taken to reduce water contact with all acid-producing material on a project - both the encapsulated material as well as the exposures on the cut slopes. This reduction can be accomplished through utilization of all or several of the following procedures:

- Construction of underdrains beneath encapsulated material.
- Construction of diversion waterways above and around encapsulated as well as excavated acid-producing material.
- Compaction and vegetation of cover material on an encapsulating embankment.
- Covering burial sites with impermeable seals.

- Locating burial sites to minimize contact with water.

Underdrains within limestone aggregate blankets placed beneath encapsulated toxic material can transmit water through an embankment with minimal wetting of the toxic material. The limestone aggregate, bound by filter

fabric, also serves as a source of alkalinity in the embankment which can reduce acidity (raise pH) of any drainage through the burial site. A major concern when installing underdrains, although not tested, is that the underdrains could enhance the diffusion of oxygen into the system.

Surface water should be diverted around all

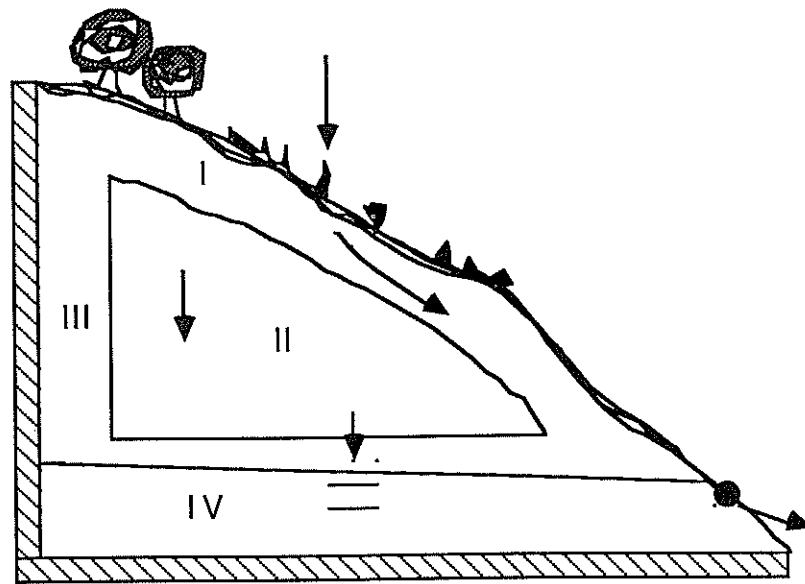


Figure 4. A model illustrating four zones in an embankment containing different concentrations of oxygen. Zone II is the area of acid-producing material where oxygen concentrations are minimized. Zones III and IV contain more porous material and, depending on water content and saturation, may or may not be highly oxidized.(5)

occurrences of acid-producing material, in burial sites as well as cut slopes. This operation can greatly reduce the amount of recharge to the ground water in those areas, thus reducing contact with the pyritic material. All road surface drainage should be intercepted and

diverted around areas containing acid-producing rocks.

The thickness and compaction of soil cover on an encapsulating embankment is very important in reducing water infiltration from precipitation events as well as the infusion of

oxygen from the atmosphere. The soil cover should be compacted to the highest density possible (90 to 95 percent of the standard Proctor maximum dry density). Mulching and seeding of the soil cover is also important. The prime purpose for establishing vegetation on an outslope is for slope stabilization, but it also can serve to reduce infiltration of air and water. Indeed, a slope that is eroded bare of its soil cover is no longer effective in reducing the influx of water and oxygen.

Impermeable seals for reducing the influx of water and oxygen into burial sites are very effective and should be given serious consideration for use where conditions permit. Many types and forms of seals are available including asphalt and tars, bentonite, concrete and cements, and geosynthetics or geomembranes. The use of such substances to cover acid-producing materials is dependent mainly upon the finished slope of the constructed burial embankment. To use these impermeable materials with a soil covering, most finished slopes would have to be 2.5:1 or flatter, otherwise slope failure is inevitable between the impermeable seal and the soil cover. Other limitations, especially with the geosynthetics include deterioration of the material and the susceptibility to being punctured.

The location of an encapsulation site should be selected to minimize contact with water. Pre-design investigations should note all water seeps as well as predict the locations of

potential water discharges based upon the structure of the bedrock and the topography. Generally the higher the site is situated on a slope, the less the potential volume of water that can come in contact with the toxic material.

The natural alkalinity that may be associated with the acid-producing materials in the rocks not only can enhance the buffering capacity needed to reduce the acidity of the drainage, but it can also impact the acidophyllic bacteria that thrive in an acidic environment and catalyze the generation of AD. The addition of alkaline material to the acid-producing environment accomplishes several goals:

- Raises pH which may result in the precipitation and filtering of some potentially harmful metals.
- Metallic precipitates may coat pyrite surfaces armoring against further chemical weathering.
- Reduces pyrite oxidation thus reducing bacterial action.

Results from experiments (appendix A) suggest that the application of pulverized agricultural lime (>95 percent CaCO_3) upon layers of compacted sulfidic material within a burial site is economical and effective in accomplishing the above goals. Soda ash was also used experimentally in tests simulating the design of a typical burial site, but was

found to produce leachates that were too alkaline. Also, soda ash is caustic to handle and not economical. Soda ash may be most effective as an ameliorant in remedial work, if a burial site were to ever fail. Table 5 is a comparison of some of the more common sources of alkalinity that have been applied in AD situations.

No economical method, to date, has been found to remove the iron-disulfides from the acid-producing materials associated with road construction projects.

Encapsulation Design

An encapsulating embankment design

utilized by the FHWA on several projects in the Appalachian Mountains of Tennessee and North Carolina has been evaluated and found to be effective in abatement of AD (see appendix A). Leachate from embankments constructed 8 years ago using this design has been analyzed as has the leachate from an experimental field tank designed to simulate the encapsulating embankment, and in both cases the effectiveness has been verified. This design is suggested for use on projects where acid-producing material must be handled on site and where the relative quantities of acid-producing material and cover material necessary for burial are possible within the constraints of the total balancing of excavated

Table 5. Comparison of ammonia to other sources of alkalinity.(6)

Chemical	Formula	1 Lb. NH ₃ equals (Lbs.)	Cost/Lb. (dollars)	Equivalent Cost (dollars)
Ammonia	NH ₃	1.00	0.24	0.24
Limestone	CaCO ₃	2.94	<0.01	0.02
Hydrated Lime	Ca(OH) ₂	2.18	0.06	0.13
Caustic Soda	NaOH	2.35	0.14	0.33
Soda Ash	Na ₂ CO ₃	3.12	0.15	0.47

material on the project. This design is shown in figure 5.

In this design pyritic material is placed in lifts of 2 ft (0.6 m) with each lift being compacted

with a sheepfoot and then blanketed with agricultural lime (95 percent CaCO₃) spread at a rate of 500 lbs per 1,000 ft² (227 kg per 93 m²). This material is placed above a 1-ft (0.3 m)

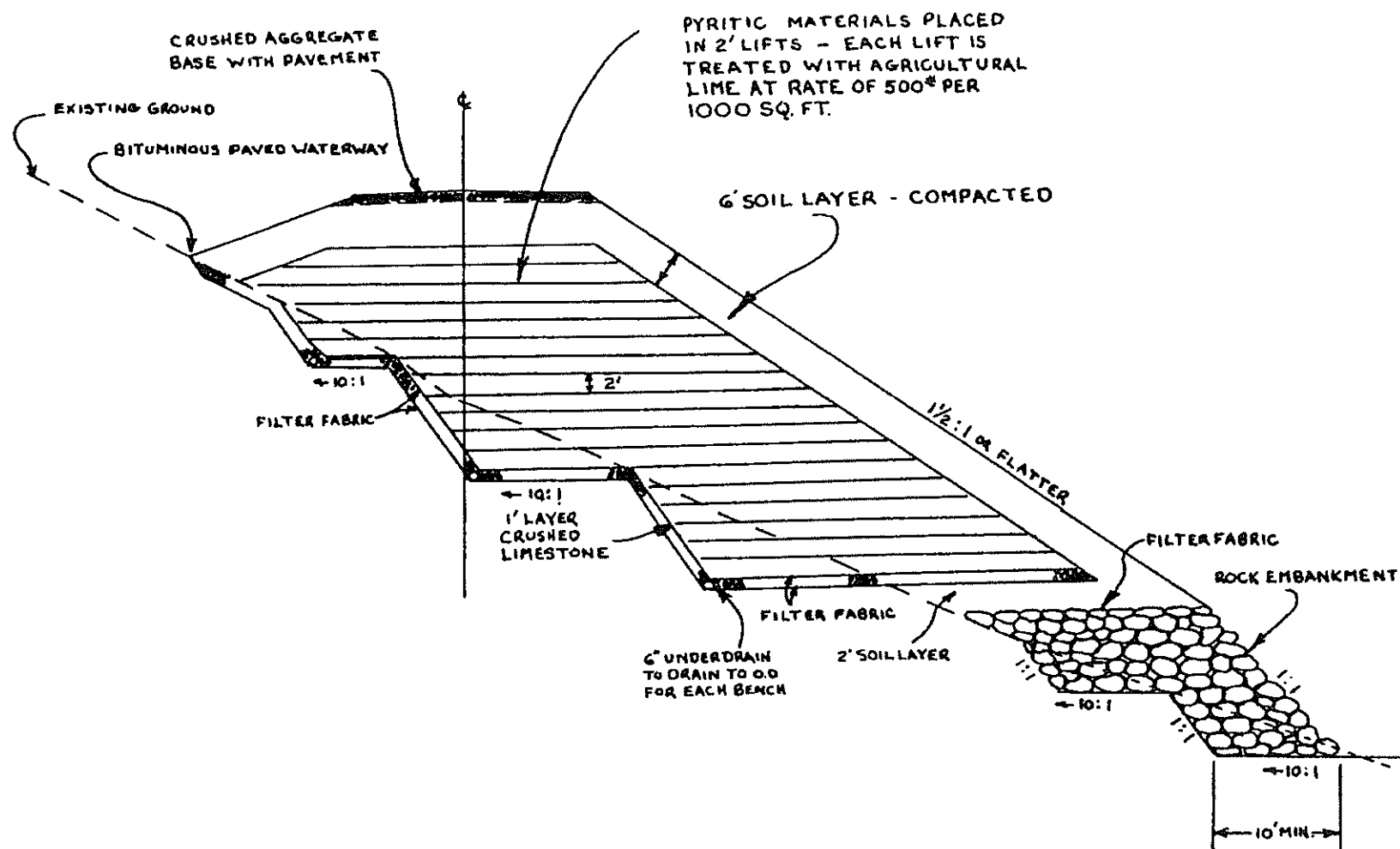


Figure 5. Encapsulation fill.

layer of limestone aggregate that is bound by filter fabric. An underdrain is placed within the limestone layer along each bench that has been cut to maintain an embankment outslope of 1.5:1 or flatter. The top and outslope of the embankment is covered with 6 ft (1.8 m) of Class A-4 soil. The outslope is brought up during the placement of each lift of acid-producing material.

This is the preferred design. It should be used in all cases where construction conditions permit. Where the quantity of acid-producing material is excessive and the quantity of cover material is limited, an alternative design is suggested. The alternative design is basically similar to the primary design above, but differs in the dimensions of the limestone aggregate blanket below the encapsulated material and the soil cover. The limestone blanket and the soil cover are reduced in thickness by 50 percent, to 6 in (150 mm) and 3 ft (1 m) respectively. This reduction permits a better ratio between the amount of acid-producing material being buried and the amount of soil cover. Experimental field tests with tanks simulating this configuration have yielded positive results for reducing AD (see appendix A). However, until more conclusive evidence is available, the alternative encapsulating design is not recommended except for special situations.

GUIDELINES FOR THE CONSTRUCTION PHASE

Segregation, handling, and storage of acid-producing materials is a continuing process during construction of a project. It is important that all freshly excavated material be inspected for pyrite, at least visually, by a trained inspector. Visually inspecting material will verify the presence of predicted acid-producing material, but it may also indicate that the quality of the rock is not acid-producing, even though it might have been predicted to be. It is important to segregate even thin layers of acid-producing material for special handling. Project engineers and inspectors must be aware of the locations of potentially problematic rocks.

As acid-producing material is encountered, it must be segregated and transported as soon as possible to a designated burial site. There the material must be placed according to design, compacted, and treated with agricultural lime. Any questionable material identified during construction should be temporarily covered with plastic film or treated with lime, and flagged until laboratory results determine its quality and its disposition on the project.

Recognition of acid-producing material and the handling, blending or treatment, and ultimate placement of that material into an embankment are the key elements in controlling AD during construction.

APPENDIX A

SULFIDE WEATHERING AND REACTION SERIES

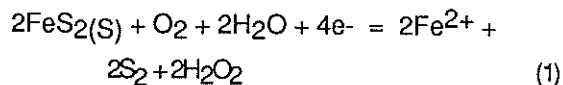
Reaction Pathways

The oxidation of sulfide minerals is a complex process involving redox reactions, electrochemical reactions and microbial catalysis. Most studies dealing with reaction pathways have utilized pyrite for experimental purposes. Only two studies were found which included a brief discussion of the inhibitory or catalytic effects of other minerals such as chalcopyrite, marcasite, pyrrhotite and sphalerite. In consideration of the data base available, the term sulfide is used throughout the remainder of this section to refer specifically to iron-bearing sulfides.

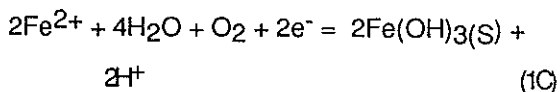
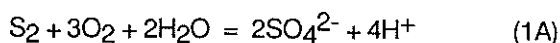
Sulfide oxidation is considered as a three phase process involving an initiation stage, an intermediate step and a propagation cycle.(7) Each of these phases contains one or more steps which contribute to the overall breakdown of sulfides and development of secondary minerals. The set of reactions and half-reactions described below show the sulfide oxidation pathway.

The initiation phase begins with sulfide oxidation in the presence of water having a neutral pH. An acidophilic bacterium (*Thiobacillus ferroxidans*) may have a very minor role in the process through direct

contact with the sulfide surface. The effects of biological organisms, however, are more pronounced in later stages and only the chemical initiation reactions are described here. The first reaction of the pathway is shown by:



The reaction products sulfur and hydrogen peroxide are unstable and rapidly oxidize or decompose. Ferrous iron oxidizes more slowly:(8)

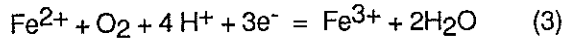


At pH values above 4.0 to 4.5, the rate limiting step of reaction 1 is the electrochemical reduction of oxygen to produce hydrogen peroxide:



The stability field relationships for the aqueous ferric - ferrous system indicates that reaction 1C proceeds as indicated as long as pH stays above 4.8.(9) As the initiation cycle progresses, the generation of acidity in reactions 1A and 1C begins to lower pH in the solution surrounding the sulfide source. Con-

sequently, the solubility of ferric iron hydroxides increases and ferric hydroxide no longer is the stable end product of reaction 1C. As the pH approaches 3.0 the reaction pathway enters the intermediate phase where ferrous iron oxidizes to ferric iron:



The oxidation rate of ferrous iron by oxygen is a function of pH at values greater than 4.5 with a second order dependence on OH^- activity as shown by the relationship:

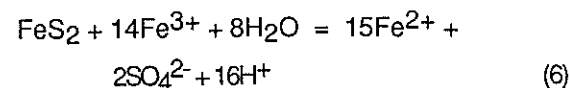
$$-d[\text{Fe}^{2+}] / dt = k [\text{Fe}^{2+}] [\text{O}_2] [\text{OH}^-]^2 \quad (4)$$

where $k_{\text{STP}} = 8.0 \times 10^{13} \text{ L}^2 \text{ mole}^{-2} \text{ atm}^{-1} \text{ min}^{-1}$.⁽⁷⁾ The half time for reaction 3 at pH = 4.5 is 300 days.⁽¹⁰⁾ At pH values of 3.5 or less, the reaction rate is independent of pH and is expressed by:

$$-d[\text{Fe}^{2+}] / dt = k [\text{Fe}^{2+}] [\text{O}_2] \quad (5)$$

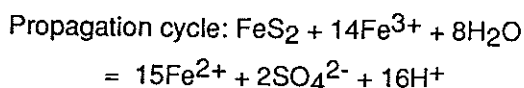
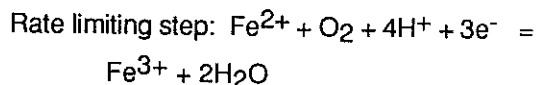
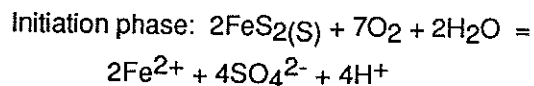
The rate constant (k_{STP}) in this case is $1.0 \times 10^{-7} \text{ atm}^{-1} \text{ min}^{-1}$ with a half time of approximately 1000 days.⁽⁷⁾

Once pH levels have decreased to around 3.0, the third phase is initiated whereby ferric iron becomes the primary oxidizing agent of unaltered sulfide minerals:



This reaction step proceeds to completion very rapidly, k_{STP} ranges from 0.389 to 17.4 day^{-1} , and is controlled by the supply of sulfides or ferric iron.⁽⁸⁾ In most natural environments a ready supply of sulfide minerals is available; therefore, the ferric iron generated in reaction 3 becomes the limiting factor. The intermediate phase (reaction 3) is the rate limiting step of the sulfide oxidation pathway due to the large discrepancy in the rates of reactions 3 and 6 under acidic conditions. Under normal circumstances, the third phase would rapidly deplete any available ferric iron generated by the rate limiting step. The production of acidity would decrease to insignificant levels very quickly given that typical ferric iron concentrations in acid mine waters are 100 mg/L or less.⁽¹¹⁾ However, at this stage the role of microorganisms becomes a major factor. Microbial catalysis by acidophilic bacteria in reaction 3 disrupts any equilibria approach in natural, aerobic settings. *Thiobacillus ferrooxidans*, *Thiobacillus thio-oxidans* and *Metallogenium* species catalyze the oxidation of ferrous iron although the latter two are essentially insignificant when in the presence of the first. *Thiobacillus* becomes active at pH values around 3.0, can tolerate acidic waters to a pH of 0.8, and increases the rate of reaction 3, the pathway limiting step, by a factor of 106.^(7,10) Reaction 6 in the presence of these bacteria, becomes a self-propagating cycle since ferric iron is continuously generated in large quantities. A summary of

the sulfide oxidation pathway is as follows:



Secondary oxidation products resulting from the weathering of sulfide minerals are principally hydrated iron sulfates or iron hydroxides. Mineral species may result either from the dehydration of soluble phases or through precipitation of insoluble products (reaction 1C). Acid mine waters containing iron in a fully oxidized state may become saturated with respect to $\text{Fe}(\text{OH})_3$ (ferrihydrite) or $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ (jarosite). Depending on pH conditions, either of these minerals can precipitate directly from the aqueous state. Additional species form either during various dehydration stages of melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) or oxidation of these compounds as in the case of copiapite ($\text{Fe}^{2+}\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$). (8) Table 6 summarizes the principal mineral phases that may be formed during the sulfide oxidation pathway.

Influence of Morphology

As expected, the oxidation rate of sulfides is

also highly dependent on crystal morphology. Sulfides in coal seams and overburden may occur in one or more of five forms: massive, mossy-pitted, euhedral crystals, cleat coatings and framboidal. (12) Framboidal sulfides are extremely fine-grained (less than 45 μm), spherical and consequently are the most reactive form. Of the iron-bearing sulfides, this crystallographic habit is almost exclusive of pyrite. Hematite has also been found to exhibit this form. Framboidal sulfides usually develop in sedimentary environments with depositional rates slow enough to permit crystallization and agglomeration of colloidal size microcrystals. Framboids have also been found in rocks ranging from volcanics to limestones. (13) Sulfide occurrences on TNFLH 1-1 (14) include euhedral forms, sheet-like masses along foliation or bedding, and disseminated. The disseminated form is most prevalent and exists in all three lithologic assemblages. The sheet-like form may be considered as analogous to cleat coatings in coal. Framboidal sulfides probably exist along with the finely-disseminated forms in the argillite and phyllite lithologies although reflected light microscopy was not used to examine hardrock samples from the project leg.

Field Studies

Studies of sulfide oxidation have universally concentrated on strictly controlled laboratory

Table 6. Principal oxidation products of sulfide weathering.(8)

Phase	Chemical	Formula	Aqueous Conditions	General Reaction
Ferrihydrite		$\text{Fe}(\text{OH})_3$	pH > 4.8	Hydrolysis of ferric iron, dis-solution of copiapite, ppt from saturated media, decomposition of jarosite
Jarosite		$\text{KFe}(\text{SO}_4)_2(\text{OH})_6$	low pH, high SO_4^{2-}	Ppt. from a saturated media
Goethite		$\text{FeO} \cdot \text{OH}$	–	Dehydration of jarosite
Hematite		Fe_2O_3	–	Dehydration of goethite, oxidation of Fe^{2+}
Melanterite		$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	high Fe^{2+} , SO_4^{2-}	Evaporation
Rozenite		$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$	–	Dehydration of melanterite
Szomolnokite		$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	–	Dehydration of melanterite, rozenite
Copiapite		$\text{Fe}^{2+}\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$	--	Oxidation and hydration of melanterite, rozenite or szomolnokite

studies with short time frames. In well-oxygenated, natural settings, one study has

determined that microbial catalysis of ferrous iron oxidation and subsequently, sulfide

oxidation, proceeds at rates very near those generated under optimum laboratory conditions.(14) Rainfall events which flush the system temporarily slow the oxidation process through dilution of Fe^{2+} and microbe populations. After the flushing event, the rate quickly increases. This study examined long-term trends in acid production both in lab and field settings.

EXPERIMENTAL METHODS

Laboratory Leaching Columns

Purpose of Lab Columns

Laboratory leaching studies have often been used to predict acid production potential in field settings. Experimental apparatus have varied in design and specific purpose, but most tests react sulfide-bearing materials with an aqueous solution and study the effluent composition over time. Literature review indicates that few studies have proceeded beyond 16 to 20 weeks. As part of this study, laboratory leaching tests were constructed to examine sulfide oxidation over a longer time frame.

The purpose of the bench scale tests was to examine effluent quality and consequently, acid production over a minimum period of 45 weeks. Changes in pH, conductivity, sulfate, total iron, Mn, Cu, Zn and Al were monitored on a weekly basis. These parameters were measured in order to determine:

1. Long-term trends in leachate quality versus time under controlled conditions;
2. If valid comparisons to, or predictions of, effluent quality generated in natural or field settings may be made on the basis of laboratory data;
3. How present predictive measures utilized on TNFLH 1-1(14) compare to laboratory generated results.

In addition, mineralogical and sulfur phase distribution examinations were conducted to determine the distribution and fate of various species during long-term oxidation of sulfides.

Design of Columns

The leaching column design chosen for the experiments was a modified version of a design developed in a previous study.(15) The construction details are shown in figure 6. The apparatus consists of a glass tube 41 in (1,040 mm) long with an inside diameter of 1.5 in (38 mm). A two-hole rubber stopper with a glass wool filter caps the base of the leaching tube. Two tubes inserted through the stopper function as an inlet and outlet for water. Perforated, 0.25 in (6.4 mm) I.D. flexible tubing runs the entire length of the tube to provide equal and complete saturation of the material while displacing most of the atmosphere inside the column out the top. A distilled water reservoir consisting of an inverted 1 L polyethylene bottle is placed near the top of each column. This reservoir has the base cut out for recharging, is stoppered at the neck, and is

graduated in approximately 100 mL increments.

Complete saturation of the sample with minimal air spaces can be attained almost instantaneously with this design. Although disaggregation of shale materials may reduce permeability to the point where water addition from the top of a column could be difficult, no permeation problems of this type were encountered. Flow of water into and out of the columns is regulated by thumbscrew hose-clamps.

Leachate collection was accomplished using 250 and 500 mL Erlenmeyer flasks. A total of

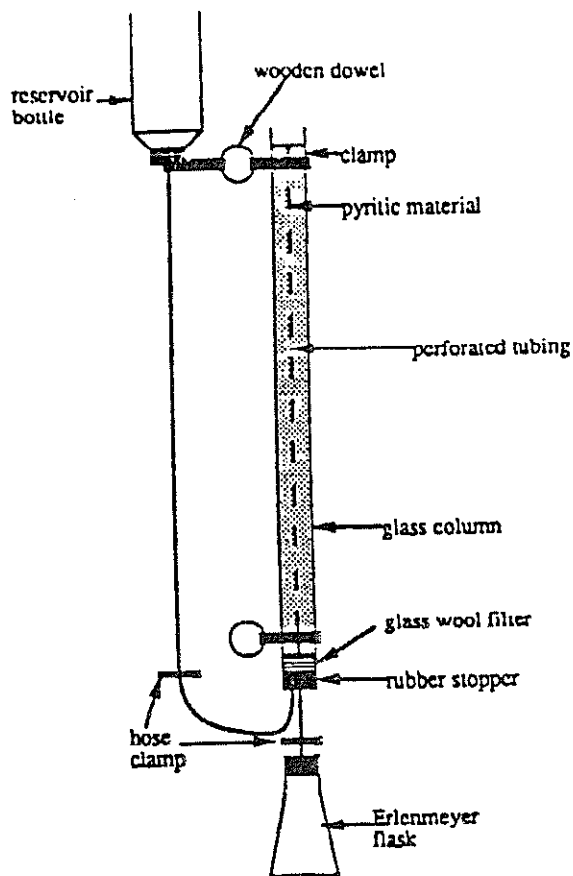


Figure 6. Laboratory leaching test schematic.

seven columns was assembled and placed on a benchtop rack for stability. Material placed in the columns was crushed by hammer under a leather cover to less than or equal to 1 in (2.5 cm). One kg (2.2 lbs) of sample was placed in each column while keeping tension on the perforated tubing to ensure that the tube was centered as much as possible and to avoid kinking. Sample material was packed lightly during assembly so that a full kilogram could be placed in each column.

The original experiment using this design determined that aeration times up to seven days between flushings do not affect leachate quality. Therefore, a leaching cycle based on a convenient time schedule was chosen. Columns were charged with deionized water (specific conductance less than 2.0 micromhos/cm³) until all material was covered. The inlet valves were sealed and the input volume recorded. Material was left saturated for 60 hours and then allowed to drain for 24 hours. Effluent was then collected, the volume measured and subsequently analyzed for the previously mentioned parameters. The aeration cycle encompassed 5 days.

Sampling Methods and Locations

Sample material for the laboratory leaching tests was obtained along four intervals on TNFLH 1-1(14) from which sulfidic rock was excavated for encapsulation. Four columns, one representing each section, were prepared from the samples. Sampling was performed

using a weighted interval method based on the exposed percentage of the three lithologic assemblages exposed along each outcrop. An excess of rock was collected from each sampling point, crushed and equal portions by weight blended to form a composite totaling 1 kg.(2.2 lbs) This method ensured that the columns contained proportions of lithologies representative of their respective intervals. Three additional columns prepared in a 1986 study were monitored for a duration equal to those prepared for this experiment. These leaching tests had been exposed to a maximum of eight cycles during 1986 and subsequently left to oxidize until the initial recharge during September 1987. Table 7 presents a summary of the leaching columns, sources and approximate percentage of lithotypes in each. HK-1 and HK-2 material was obtained from pyritic outcrops east of TNFLH 1-1(14), and MGQ was obtained from a road base source quarry to the west of the segment. HK-2 was initially charged in 1986 with calcium carbonate saturated water to simulate chemical injection mitigation methods.

Field Leaching Studies

Purpose of Field Tests

Field leaching experiments were constructed to examine the effectiveness of present encapsulation techniques used on TNFLH 1-1(14). Additional objectives of these field

studies included the utilization of the leach tests to attempt to develop a more cost effective method for sulfidic material encapsulation and to project chemical trends within present sites. Comparisons of tank leachates to actual encapsulation site effluents were examined to determine the effectiveness of each model in reducing toxicity in relation to untreated waters. Variations in effluent quality due to seasonal changes and rainfall inputs were also examined.

General Design

For the purpose of accurately assessing an encapsulation site, a model was created which simulated the internal roadfill design as closely as possible. Variations were then made in the amounts, chemical composition and position of the representative limestone aggregate layer and in the amount of topsoil cover. Each model was constructed using 30 gal (100 L) polyethylene drums and incorporated approximately 350 lb (160 kg) of sulfidic material. This volume was large enough to allow a realistic simulation, yet be constructed within the constraints of time and cost. The dimensions of the drum corresponded to a vertical scale factor of approximately 10 as calculated from an average fill depth of 30 ft (9 m) determined through measurements and borehole data. The dimensions of each drum were a height of 3.0 ft (0.9 m) by 1.7 ft (0.5 m) in diameter. The initial model, therefore, contained limestone aggregate in a basal

Table 7. Input materials for laboratory leaching tests.

Column	Material Source	Percent Lithotype	NNP of Source.
HK-1	Exposures along Hemlock Knob	Predominantly argillite	-50 tons CaCO ₃ /1,000tons
HK-2	Exposures along Hemlock Knob	Predominantly argillite	-50 tons CaCO ₃ /1,000tons
MGQ	Road base source quarry	Meta-sandstone	+50 tons CaCO ₃ /1,000 tons
Comp A	959+30 - 969+30	40% meta-sandstone 60% argillite	-8 tons CaCO ₃ /1,000 tons
Comp B	988+00 - 990+50	50% meta-sandstone 50% argillite	-35 tonsCaCO ₃ /1,000 tons
Comp C	996+50 - 998+50	25% meta-sandstone 75% argillite	-43 tons CaCO ₃ /1,000 tons
Comp D	1048+00 - 1058+00	80% meta-sandstone 20% argillite	-18 tons CaCO ₃ /1,000 tons

configuration that was 0.2 ft (60 mm) thick between BIDIM-U14 filter fabric. Sulfidic material was placed in 0.2 ft (60 mm) thick lifts with agricultural lime application between each layer. Lime application rates used during fill construction were about 200 gm/ft² (6.7 kg/m²). Although this value was not strictly scaled down, lime application utilized in the

tank design was roughly equivalent to 20 gm/layer or 9 gm/ft². This rate provided a sufficient cover of the pyritic material. A topsoil cover 0.6 ft (180 mm) in thickness capped the model. Drainage was provided by a PVC nozzle installed in the base of the tank. Lids, having a large opening in the center, were fastened on each model with wire. The edge

of the lid opening protruded approximately 2 in (50 mm) over the encapsulated model. This design insured that rainfall contacted as much material as possible without merely filtering down the inside wall of the drum (figure 7). Test effluents were collected in 1.0 gal (3.8L) polyethylene bottles. All leaching experiments were constructed near TNFLH 1-1(14) and immediately adjacent to a rain gauge in order to monitor the amount of rainfall that the models received.

Variations in the Model

Nine leaching models were constructed for this study. Seven variations of the encapsulation method were designed using similar source material. One tank was left empty to

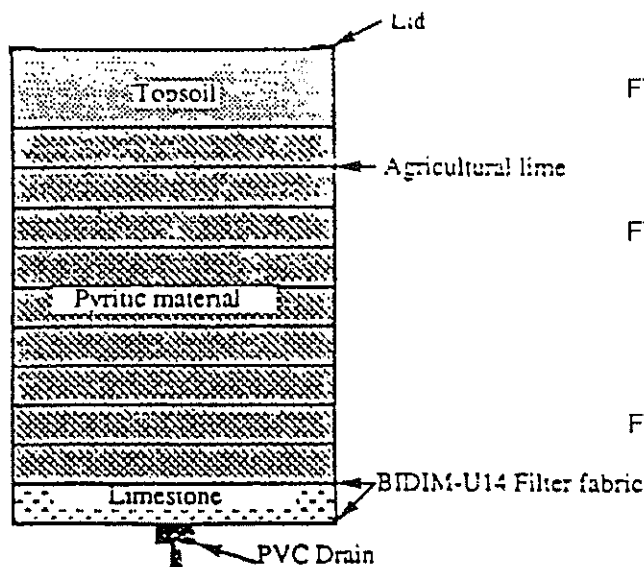


Figure 7. Field leaching test schematic.

serve as a prototype and to collect rainwater.

Another tank incorporated sulfidic material from a nearby source other than TNFLH 1-1(14).

The models were designed as follows:

- FT-0: Prototype and empty tank for the collection of rainwater.
- FT-1: Control model containing only sulfidic material.
- FT-2: Original model based on currently used encapsulation site design, with a full compliment of basal aggregate, agricultural lime and topsoil.
- FT-3: Model containing a full compliment of limestone aggregate and topsoil with the limestone aggregate buffer layer placed at the top of the model.
- FT-4: Model similar to FT-2, but featuring a 30% reduction in the amount of basal limestone aggregate.
- FT-5: Model similar to FT-2, but featuring a 60% reduction in the amount of basal limestone aggregate.
- FT-6: Model similar to FT-2, but featuring a 50% reduction in the amount of topsoil cover, full compliment of basal limestone aggregate.
- FT-7: Model featuring a buffer layer composed of approximately 500 gm (1.1 lb) of NaCO_3 briquettes and a full compliment of topsoil cover.
- FT-8: Untreated material from a U.S. Forest Service access road containing coarsely crystalline sulfide minerals.

Sampling

Material for each model, except FT-8, was obtained from the same 250 ft (76 m) roadcut from which laboratory composite B was formed (refer to table 7). This section was chosen because approximately equal percentages of the various lithologies were represented in the section. In addition, NNP values show that this section was one having a high potential for acid production on TNFLH 1-1(14). An estimated 4,000 yd³ (3,060 m³) of rock from this cut were encapsulated during road construction. Water samples from the fill containing this material were used for baseline leachate quality comparisons. A weighted interval sampling technique was used to obtain samples with specific points being equal to those used to construct Comp B. Although no accurate assessment of particle size used in actual fill construction was available, sampled rock was crushed by hammer and the size fraction less than or equal to 4 in (100 mm) was retained. Any material which showed signs of weathering was discarded. Retained sample was mixed at random, by hand, during construction of the models.

Field Samples

Purpose and Locations

Surface water samples were collected at several locations along TNFLH 1-1(14). These samples provided baseline water quality

measurements for both the lab and field leaching experiments. They also illustrated typical acidic effluent values in true field settings and aided in the evaluation of present FHWA remedial action measures.

Table 8 gives the sampling locations, descriptions of the locations and sampling periodicity for each point examined during the study. Samples F-996+50-UD and HK-SR were the primary field sampling localities. F-996+50-UD represents effluents emitting directly from the encapsulation site chosen for correlation with the field models. This fill was selected due to the accessibility of an under-drain with discharge sufficient for sampling. In addition, approximately 50 percent of the pyritic volume encapsulated at this site originated from the interval in which material was obtained for construction of the field tanks. HK-SR, in addition to the other sampling points, provides an indication of water quality resulting from unimpeded sulfide oxidation in a fully aerated environment. A sampling periodicity of 30 days maximum was attempted for F-996+50-UD and HK-SR; however, due to extremely low rainfall amounts during portions of the study period, this criterion could not always be met.

Miscellaneous Studies

Cores

Four boreholes using a hollow-stem power

Table 8. Locations and descriptions of field sampling points.

Sample ID	Location	Description	Sampling Periodicity
F-996+50-UD	Encapsulation site	Mouth of under-drain at base of fill at 996+50 on TNFLH 1-1 (14)	30 days
HK-SR	Near crest of Hemlock Knob approximately 2 miles east of TNFLH 1-1 (14)	Surface drainage ditch along base of roadcut	30 days
A-OR, A-SR	959+30	Surface drainage ditch and outcrop runoff along base of roadcut	Once
C-OR	996+50	Runoff from outcrop face	Twice
D-SR	1052+00	Surface drainage ditch along base of roadcut	Twice

auger and 2-in (50 mm) split spoon sampler were drilled into encapsulation sites along TNFLH 1-1(14) and at one location east of the project. Boreholes 2, 3 and 4 were placed into fills containing the same source materials used for the construction of lab columns Comp A, Comp B, Comp C and all field tanks except FT-8. BH-1 was drilled into a fill approximately 3 mi (4.8 km) east of the project. This particular fill contained pyritic material that was untreated

prior to burial and was used as a baseline comparison for the remaining cores.

The purpose of the boreholes was to penetrate the full depth of the encapsulation site through the limestone underblanket. This was only accomplished in BH-3. Pertinent information gathered from the cores included the state of sulfide oxidation and material degradation in encapsulation sites and untreated fills; condition of the limestone

buffer layer; and mineralogical assessment of both primary and secondary phases present in the encapsulated material.

Mineralogical Characterization

A mineralogical characterization using XRD and a binocular microscope was performed on rock samples obtained during leach test sampling and borehole drilling. X-ray diffraction analyses were conducted on composite packmount samples from each borehole in addition to composites from the Hemlock Knob location and each interval from which lab leach tests materials were obtained. Also, upon dismantling of the laboratory leaching columns, sufficient oxidation products were present in HK-1, HK-2 and Comp C to allow examination. The leached material from these column experiments was sampled by cone and quarter method, the sample placed in a polyethylene bottle, and agitated by ultrasound for a minimum of two hours. The liberated portion of the oxidation products was decanted and an elutriated mount was prepared for X-ray analysis.

The mineralogical examination of these samples allowed comparisons to be made between pre- and post-oxidation phases present in both treated and untreated fills, as well as in laboratory tests. The investigation of leaching material mineralogies permitted the identification of secondary phases resulting from oxidation which coat the rock material. These phases are of particular interest in that

they serve to armor both pyritic material and, in fills, any limestone buffer blanket that is installed to neutralize acid drainage. The effects of coating can decrease the oxidation of pyrite through reduced O₂ contact, and can decrease the buffer capacity of limestone aggregate. If secondary phases are precipitated in sufficient quantity, they begin to fill interstitial voids within a roadfill. This void filling decreases the infiltration capacity of an encapsulation site and lowers O₂ content available for sulfide oxidation.

Sulfur Speciation Study

A sulfur speciation study was undertaken to determine several parameters in pre- and post-leached materials in the bench scale tests. This procedure allows the calculation of percent sulfur present as sulfide, sulfate and organic forms.(2) All leached rock except that in MGQ and Comp B was examined. The percentage reductions in total sulfur in these columns during the course of the tests was also determined. The amount of sulfur present as these three forms was examined in unleached material from Comp C for comparative purposes.

Analytical Methods and Measured Parameters

Water samples collected for this study were analyzed for volume collected (with the exception of surface stream samples), pH, conductivity, sulfate, acidity, Al, total Fe, Mn,

Cu, and Zn.

Standard procedures for field sampling were followed when collecting surface water and fill effluent samples. These samples were collected in 1 litre polyethylene bottles. All effluents were separated into two fractions. The first was left unfiltered for pH, conductivity and acidity measurements. The second fraction was vacuum filtered through a 0.45 micron membrane filter as soon as possible after collection in order to remove all particulates. This fraction was acidified to a pH of less than 2.0 with ultrapure HNO_3 and refrigerated at 40°C (390°F) for future analysis of dissolved metals.

Volume measurements conducted on field tank effluents and laboratory leachates were done using a graduated polyethylene cylinder. The cylinder was rinsed with deionized water followed by a rinse with dilute HCl and several rinses with deionized water between readings to avoid cross contamination of samples.

Measurements of pH were made using a Beckman Electromate Model 100001 pH meter with an Orion combination electrode. A Hach conductivity meter was used for specific conductance measurements.

Sulfate was determined using a barium sulfate turbidity technique in conjunction with a Hach DR/2 benchtop spectrophotometer.⁽¹⁸⁾ This procedure involved the separation of 50 mL of filtered effluent into two 25 mL fractions which were placed into cuvetts. One portion was used as a blank and left un-

treated. Barium chloride indicator was added to the second cuvet and allowed to react for 5 minutes. After the reaction phase, the blank absorbance was measured on the instrument and calibrated to represent zero. The use of the blank compensated for any absorbance due to coloration of the effluents. The treated cuvet absorbance was then measured and the sulfate concentration determined from a calibrated scale.

Acidity measurements were made using titrimetric methods.⁽¹⁸⁾ A 50 mL aliquot of unfiltered water was used for analysis. The sample was acidified to a pH of less than 4.0 with 0.02 N H_2SO_4 , if the original pH reading was above this value. Samples having pH values less than 4.0 were not acidified. Two to three drops of 30 percent H_2O_2 were added to each sample and heated to digest organics. Samples were cooled and titrated using 0.1N NaOH and Fisher Scientific automated instrumentation to an inflection endpoint pH of 8.3. Acidity is represented as mg/L CaCO_3 through unit recalculations. Positive acidity values indicate acidic water, whereas a negative acidity indicates excess alkalinity.

Aluminum was measured using two methods. The procedure used for most samples was an absorptiometric technique utilizing pyrocatechol violet as an indicator.⁽¹⁷⁾ This wet chemical technique provides rapid turnaround analysis of samples with Al concentrations as low as $42\text{ }\mu\text{g/L}$. The method has some limitations due to chemical

interference by high Fe concentrations. Effluents from FT-1, FT-8, C-OR and some samples at HK-SR exhibited Fe interference too high for effective analysis. Aluminum in these effluents was measured using flameless atomic absorption (AA) via carbon rod analyzer (CRA). CRA avoids many of the chemical interference problems associated with flame AA or colorimetric methods.⁽¹⁵⁾ However, the considerable time, cost and rigorous analytical program design requirements precluded the use of a CRA for aluminum analysis in all effluents.

The remaining dissolved metals were determined by flame AA using a Varian 475 double beam spectrophotometer. Analytical program guidelines were established for each specific metal to reduce interferences resulting from chemical or physical interactions between species or the flame and analyte.^(18,19)

An analytical quality assurance (QA) program was followed for each respective parameter measured in the effluents. The program ensured that results were as accurate and precise as possible and reduced the chances of contamination. All labware and sample bottles used during the study were cleaned using a standard multistep washing procedure involving a detergent wash, potable water rinse, deionized water rinse, 10 percent HCl rinse and several final washes with deionized or distilled-deionized water. Clean sample bottles, prior to use for collection or storage of

effluents, were rinsed with sample as a final precaution.

Conductivity and pH equipment was calibrated using standard solutions prior to a battery of analyses. Probes were rinsed with deionized water and wiped dry between readings. Conductivity and pH readings were taken in the field when possible. If samples were frozen or weather conditions unfavorable, these parameters were measured after return to the laboratory.

Sulfate standards were analyzed for QA purposes during each analytical run for that parameter. The dissolved metals analysis incorporated both single and multielement standards to construct calibration curves and check the accuracy of the calibration equations on a daily basis. During AA runs, two standards were run to every 10 samples to maintain a constant check on accuracy. To examine laboratory QA as a whole, a set of certified, multielement, commercial water standards were purchased through Environmental Resource Associates of Arvada, Colorado and analyzed. This process allowed inter-laboratory comparisons to be made and served as a final accuracy and precision check for all analytical procedures.

RESULTS OF METHODS

Lab Columns

Data Trends in Effluents

The bench scale leaching tests were conducted for 45 cycles. All columns were initially charged on 9-4-87. Testing ended on 7-14-88. Comparisons of the measured parameters over time indicate that leachates from all columns attained a constant chemical quality very rapidly. Effluents generally had high initial values of chemical parameters which decreased until stabilization occurred. The initial stabilization period for most tests was 1 to 5 cycles. All columns had reached a restricted range of values after 10 cycles. All of the parameters measured for this study, with the exception of Aluminum (Al), followed this trend. Aluminum values exhibited a reverse trend with concentrations increasing until stabilization further into the experimental program. The parameters showing the least fluctuation over time were pH, conductivity and sulfate (figures 8 - 13). The consistent drop in conductivity levels seen in HK-1 from cycle 40 to cycle 43 is not representative of the general trend. A plausible explanation for the decrease cannot be determined from experimental records. Acidity values demonstrated moderate variance (figures 14 and 15). A significant spike in acidity levels was observed at cycle 41 for HK-1. The increase is not consistent with the decrease of conductivity

values over the same period and may be attributable to an error in the analysis.

Aluminum, iron and zinc concentrations, when above detection levels, had the greatest variance from cycle to cycle (figures 16 - 19). Aluminum levels in MGQ (see table 7) effluents were consistently below detection and are not included in the data plots. The sharp increase in Zn concentrations for HK-1 at cycle 33 may be attributable to analytical error. Copper concentrations were below detection in all leachates. Manganese values were present above detection levels over time only in Comp B and Comp C. Comp B began with concentrations at 3.7 mg/L which decreased to less than 1.0 mg/L by cycle 33. Comp C began at 4.8 mg/L and by cycle 41 had decreased to below detection levels.

The patterns over time seen with all species except Al are probably due to the rapid oxidation of abundant fine material generated by pulverization of the rock material. The great surface area results in rapid depletion of the sulfide source in the fines during the first few cycles. This depletion causes high initial concentrations of sulfate, acidity and dissolved metals which decrease in proportion to decreasing amounts of unoxidized silt- to fine-sand sized sulfidic material. The initial oxidation also drives the pH of interstitial water down rapidly during the first few cycles. Aluminum concentrations would not be expected to be high initially. The increase in Al solubility occurs in response to the decrease

in pH. Therefore, 2 to 3 cycles are required in order for substantial Al to be generated from aluminosilicate minerals which are the primary source.

Sulfur Speciation and Depletion

Following the leaching experiments, sulfur phase distribution was determined for the leached materials from all columns except Comp B and MGQ. MGQ was not analyzed since leaching studies indicated the initial absence of sulfides. Comp B remained on line for continued monitoring at the close of this study and subsequently was not examined. For baseline comparisons, sulfur phase distributions in unleached materials comprising Comp C were calculated. The method used for these experiments allows the calculation of sulfur present as pyritic (sulfide), sulfate and organically-bound phases.⁽²⁾ A series of acid leaching steps using HCl and HNO₃, with sulfur analysis via a LECO furnace between leachings, was used to determine the distribution. The analysis of unleached materials shows that approximately 50 percent of the total sulfur present is in the form of sulfides. A surprisingly high percentage was bound with organics; however, the value is not unreasonable given that these rocks were 75 percent argillite and probably had a high initial organic content. Sandstone dominated materials would probably show less of this phase. Substantial reductions in the amount of sulfide sulfur were observed in the leached materials.

Columns HK-1 and HK-2 show that nearly all of this phase had oxidized after about 2 years of oxidation alternating with leaching. The total sulfur content was still quite high and almost all of that which remained was bound with organic materials. Since Comp C materials show that the organic sulfur remains constant in pre-versus post-leaching rock, a valid assumption might be that the high values in HK-1 and HK-2 reflect relative increases, with respect to decreases in the other types, rather than true redistribution into this form. The oxidizing environment within the columns would be expected to preclude formation of significant organic sulfur. Leached materials from the remaining columns indicate that approximately one-half of the total initial sulfur content was leached from the columns over a period of 45 weeks. The significance of these findings in relation to acid production is discussed below.

Mineralogical Changes

Pre-leaching and post-leaching mineralogical characterizations were performed on the Hemlock Knob and Comp C materials. Columns MGQ, Comp A, and Comp D were not analyzed due to the lack of sufficient oxidation products to provide enough sample for elutriated X-ray mounts. Comp B was not analyzed since leaching experiments with this column continued at the close of the study. HK-1 and HK-2 both contained alteration products sufficient to cement the material together and coat the walls of the leaching

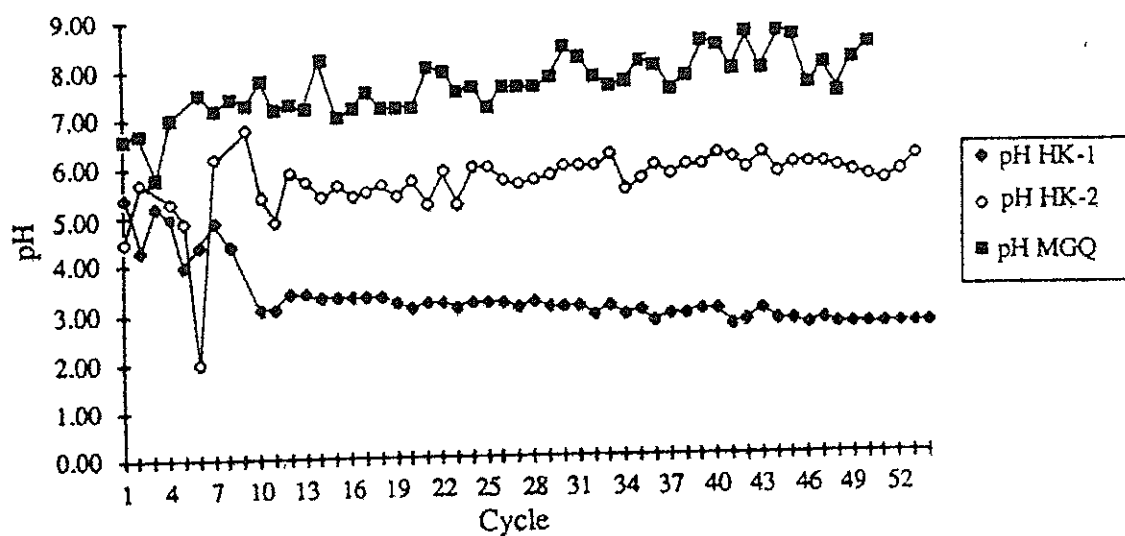


Figure 8. Plot of pH versus cycle for columns HK-1, HK-2, and MGQ

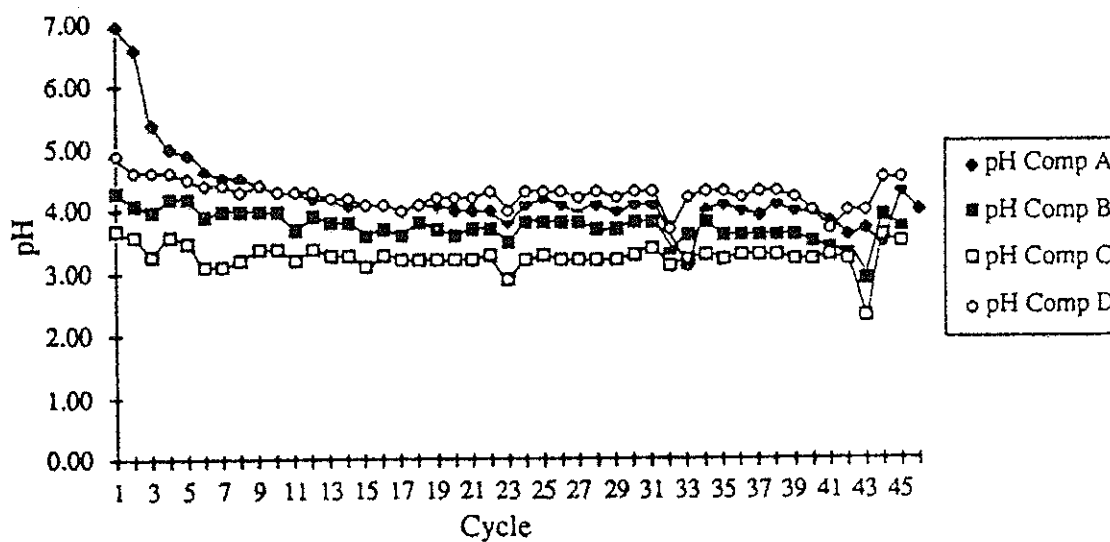


Figure 9. Plot of pH versus cycle for columns Comp A, Comp B, Comp C and Comp D.

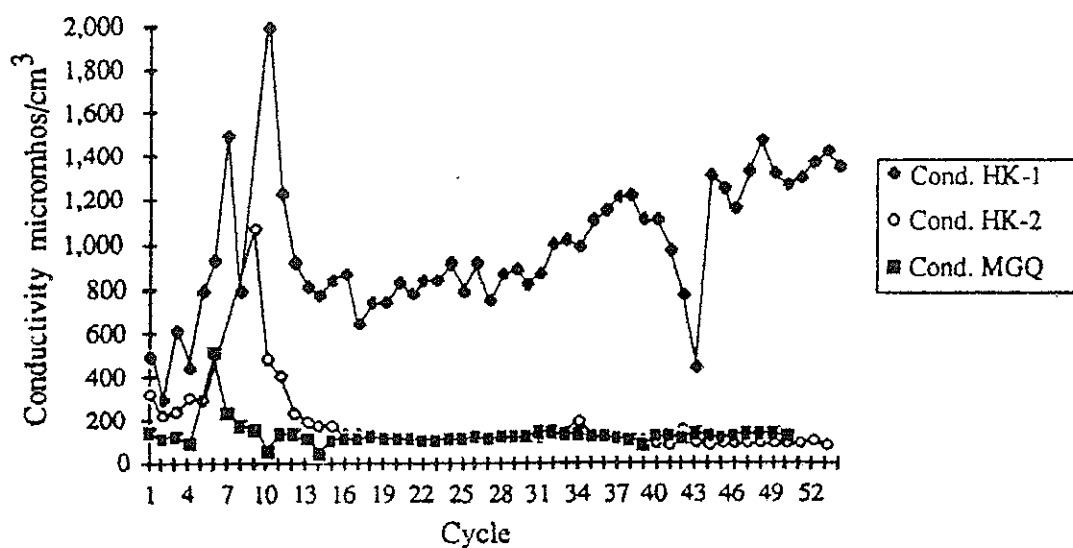


Figure 10. Plot of conductivity versus cycle for columns HK-1, HK-2 and MGQ.

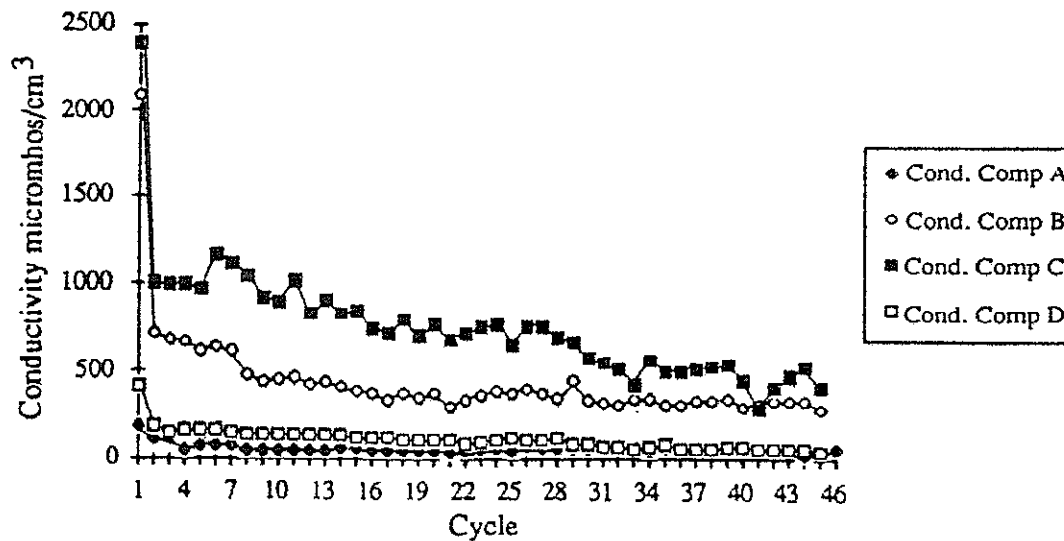


Figure 11. Plot of conductivity versus cycle for columns Comp A, Comp B, Comp C and Comp D.

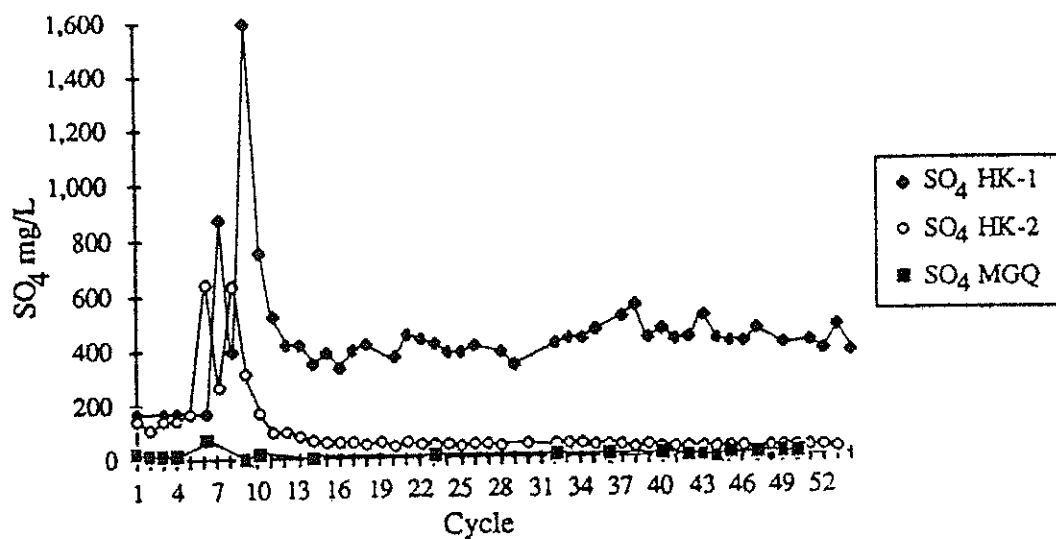


Figure 12. Plot of sulfate versus cycle for columns HK-1, HK-2 and MGQ.

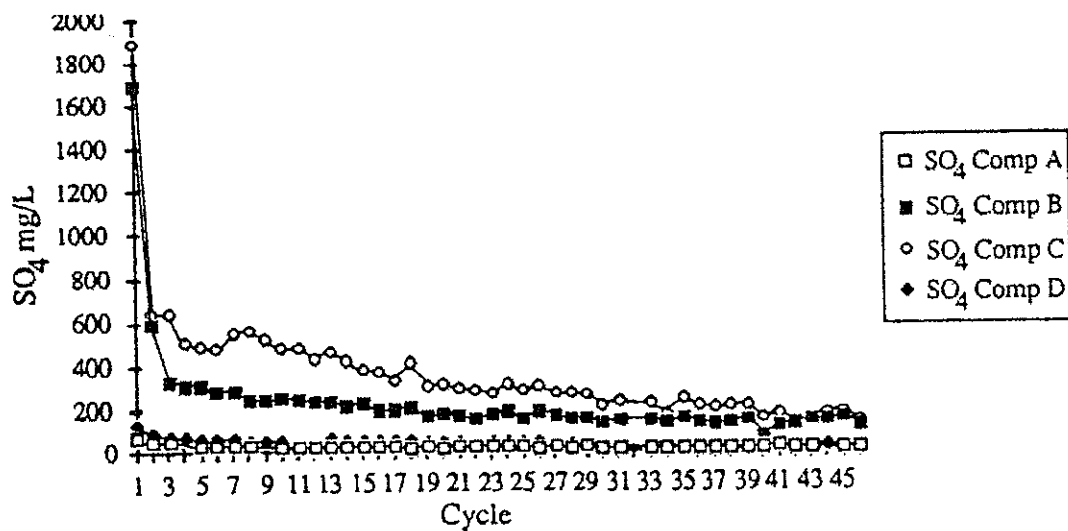


Figure 13. Plot of sulfate versus cycle for columns Comp A, Comp B, Comp C and Comp D.

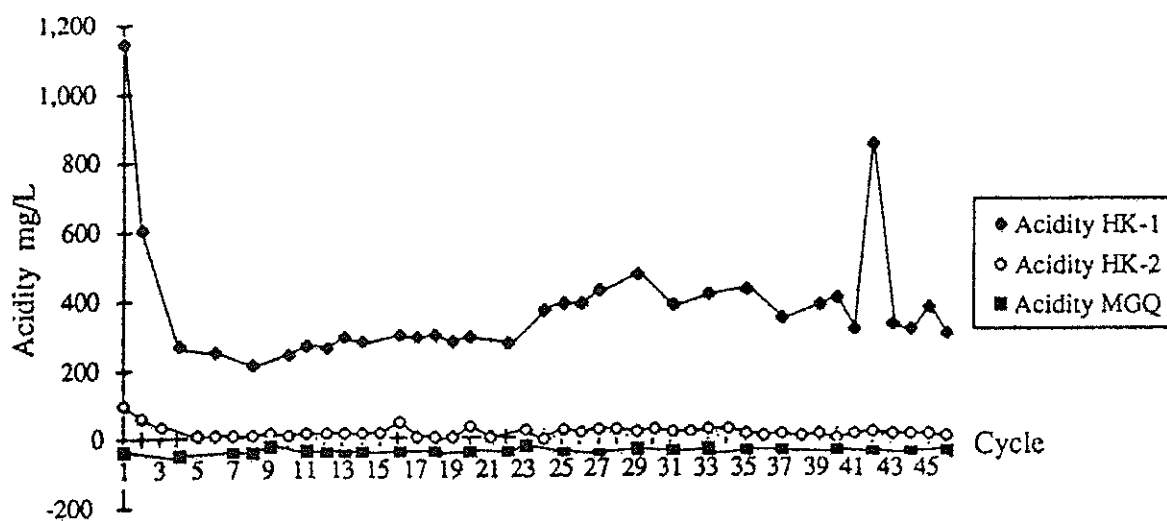


Figure 14. Plot of acidity versus cycle for columns HK-1, HK-2 and MGQ.

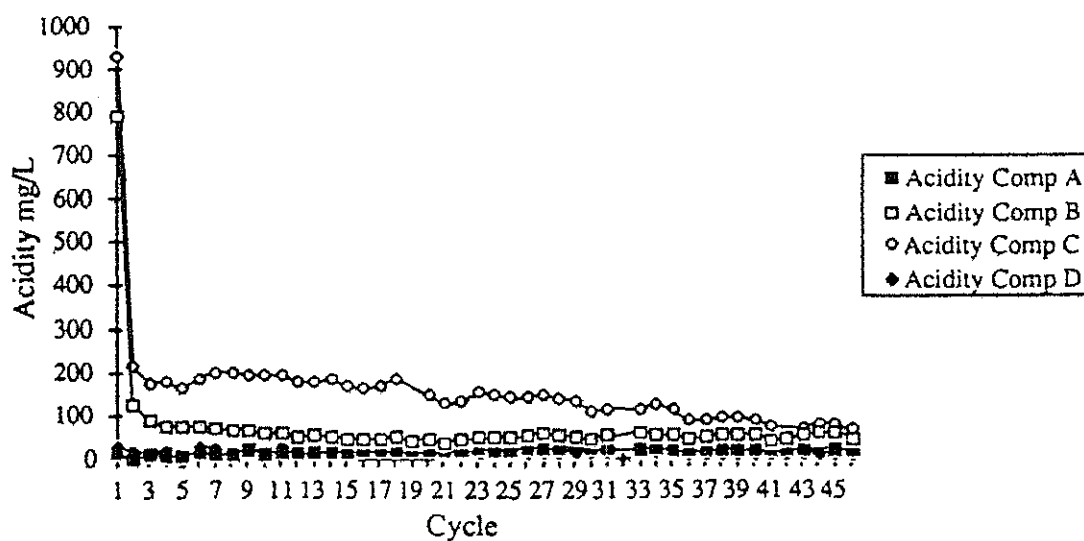


Figure 15. Plot of acidity versus cycle for columns Comp A, Comp B, Comp C and Comp D.

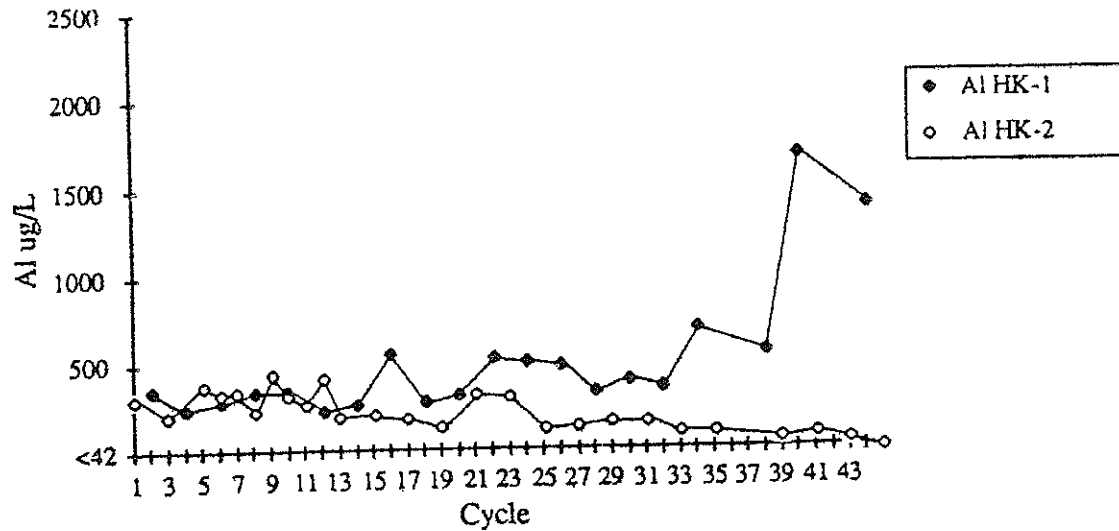
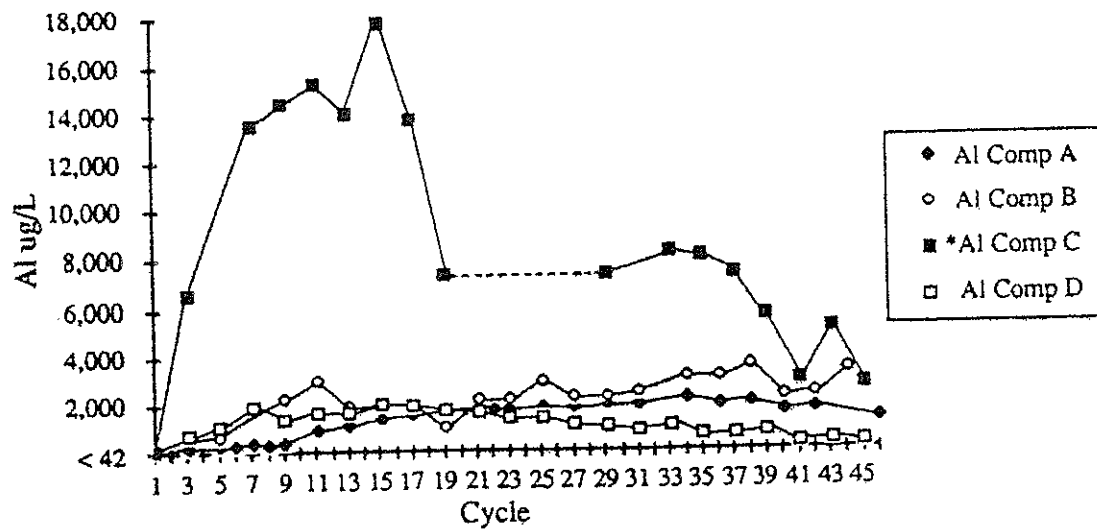


Figure 16. Plot of aluminum versus cycle for columns HK-1 and HK-2.



* - - - = Gap in analytical sequence due to insufficient volume for analysis

Figure 17. Plot of aluminum versus cycle for columns Comp A, Comp B, Comp C and Comp D.

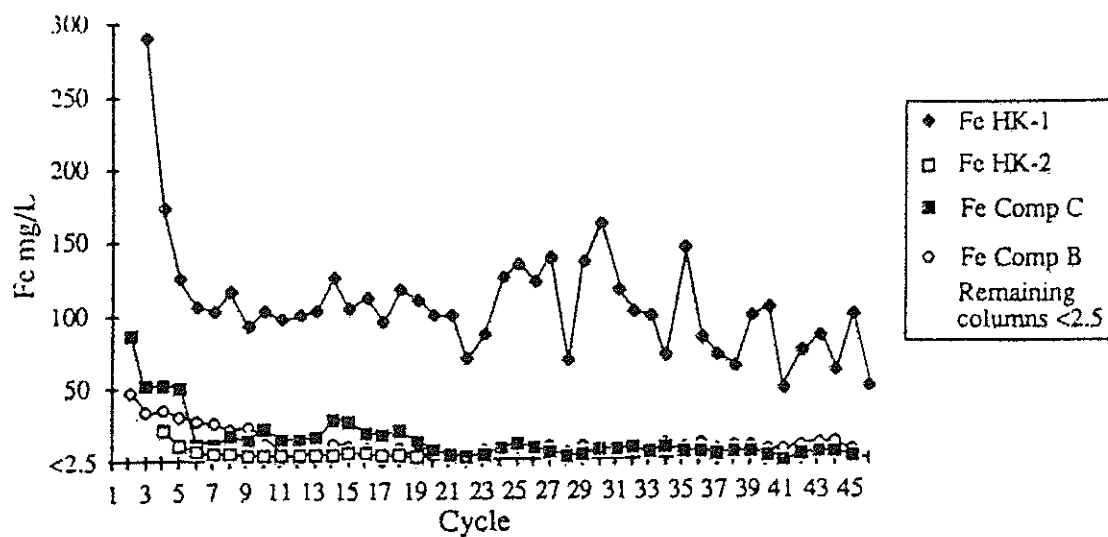


Figure 18. Plot of iron versus cycle for columns HK-1, HK-2, Comp C, and Comp B.

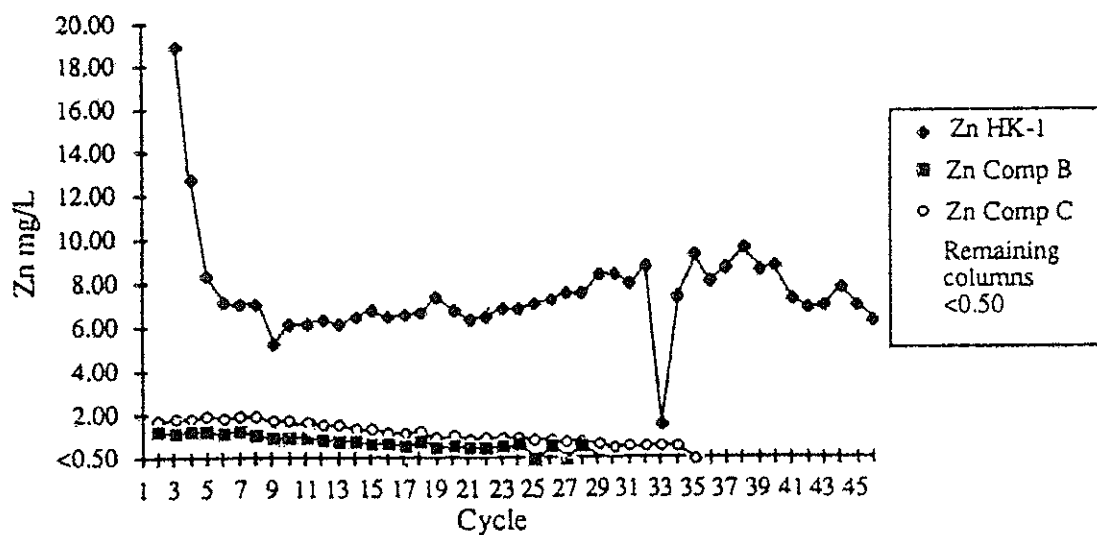


Figure 19. Plot of zinc versus cycle for columns HK-1, Comp B, and Comp C.

tube. Comp C, while not cemented, exhibited widespread particle coatings and material degradation.

The mineral identification was performed using X-ray diffraction and binocular microscope examinations. The variety of phases present in the sample materials resulted in complex X-ray patterns which proved difficult to interpret. Mineral identification was based on five or more d-spacings which matched exactly or within reasonable error tolerances. If between three and five d-spacings were matched, and presence of the potential phase feasible, the identification was assumed to be tentative. Several unidentified lines remained in each pattern after the characterization. All samples were analyzed using Cu K alpha radiation on a Norelco diffractometer. A one degree per minute rotation was used to generate the patterns. Table 9 shows the results of the characterization for unleached and leached materials from Hemlock Knob and table 10 gives the comparisons for Comp C materials. The post-leaching secondary phases identified are those that generally are expected to form during oxidation of sulfide and feldspar minerals. One unexpected phase prevalent in the leached material was yavapaiite. The abundance of potassium phases such as jarosite and yavapaiite indicates the presence of a significant source for this cation within the rocks used in the leaching systems. A possible potassium source is the dissolution of feldspar minerals and

muscovite.

Field Tanks

Data Trends in Effluents

All variations of the encapsulation models, with the exception of FT-0, FT-7 and FT-8, were placed into service within a 60 day period beginning 9-10-87 and ending 11-7-87. FT-0 began service on 8-27-87, FT-1 on 12-23-87 and FT-8 on 1-14-88. All data plots presented in this section represent the same amount of real time within the range outlined above. However, the number of collections varied for each of the models due to slightly different responses to rainfall inputs, overturned or burst collection vessels and one incidence of vandalism. Over time, pH in all variations featuring treatment amendments, with the exception of FT-7 (Na_2CO_3 buffer), tends to approach a common range of 6.8 to 8.0 (figures 20 and 21). Values of pH in FT-3, containing the limestone aggregate layer at the top of the sulfidic rock volume, were slightly lower and demonstrated more variability. FT-1 and FT-8, both containing untreated material, show a steady decline in pH until stabilization at values from 2.8 to 3.4 and 2.0 to 2.4 respectively.

FT-7 produced highly alkaline effluents unsuitable for most analyses although the amount of buffer material was relatively small (500 gm). Typical pH and conductivity values for this model are 10.0 to 11.0 and 207,000

Table 9. Mineralogical characterization for Hemlock Knob materials.

HK-Unleached	HK-1 Leached	HK-2 Leached	Formula
<u>Identified:</u>	<u>Identified:</u>	<u>Identified:</u>	
Quartz	Quartz	Quartz	SiO ₂
Muscovite	Muscovite	Muscovite	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂
Albite	–	–	NaAlSi ₃ O ₈
Marcasite	–	–	FeS ₂
–	Kaolinite	Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄
–	Yavapaiite	–	KFe(SO ₄) ₂
–	Jarosite	–	KFe(SO ₄) ₂ (OH) ₆
–	–	Copiapite	Fe ²⁺ +Fe ³⁺ ₄ (SO ₄) ₆ (OH) ₂ · 20H ₂ O
<u>Tentative:</u>	<u>Tentative:</u>	<u>Tentative:</u>	
–	Copiapite	--	Fe ²⁺ +Fe ³⁺ ₄ (SO ₄) ₆ (OH) ₂ · 20H ₂ O
–	Melanterite	Melanterite	FeSO ₄ · 7H ₂ O
–	Ferrihydrite	Ferrihydrite	Fe(OH) ₃
–	Illite	Illite	(H ₃ O,K) _y (Al ₄ .Fe ₄ .Mg ₄ .Mg ₆)- (Si _{8-y} .Al _y)O ₂₂ (OH) ₄
–	–	Jarosite	KFe(SO ₄) ₂ (OH) ₆

micromhos respectively. Substantial improvement in conductivity was seen in the most recent samples. No other parameters were measured for this model.

Conductivity, sulfate and acidity show trends similar to that of pH. These parameters demonstrate significant variability in the first few samples collected. Stabilization at a restricted range of values occurred after the first few rainfall flushing events. In general, FT-2, the original model, had somewhat lower conductance and sulfate values than the

remainder of the tanks. FT-3, having the limestone layer at the top of the pyritic volume, did not exhibit a substantial recovery period with respect to conductance, sulfate and acidity values. FT-2 and FT-6 (50% topsoil reduction) seem to show the most resistance to fluctuations in species concentrations while FT-3, FT-4 (30% aggregate reduction) and FT-5 (60% aggregate reduction) values showed more variability. Figures 22 to 27 show the patterns of effluent quality, with respect to these variables in the lime-treated models.

Table 10. Mineralogical characterization for Comp C Materials.

Comp C Unleached <u>Identified:</u>	Comp C Leached <u>Identified:</u>	Formula
Quartz	—	SiO ₂
Clinocllore	Clinocllore	(Mg,Fe ²⁺ ,Al) ₃ (Si,Al) ₂ O ₅ (OH) ₄
Illite	Illite	(H ₃ O,K) _y (Al ₄ .Fe ₄ .Mg ₄ .Mg ₆) ⁻ (Si _{8-y} .Al _y)O ₂₂ (OH) ₄
Muscovite	—	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂
Augite	—	(Ca,Na)(Mg,Fe ²⁺ ,Al)(Si,Al) ₂ O ₆
Albite	—	NaAlSi ₃ O ₈
—	Yavapaiite	KFe(SO ₄) ₂
—	Copiapite	Fe ²⁺ Fe ³⁺ ₄ (SO ₄) ₆ (OH) ₂ · 20H ₂ O
—	Alunite	KAl ₃ (SO ₄) ₂ (OH) ₆
<u>Tentative:</u>	<u>Tentative:</u>	
Pyrite	—	FeS ₂
Smythite	—	(Fe,Ni) ₉ S ₁₁
—	Jarosite	KFe(SO ₄) ₂ (OH) ₆
—	Diaspore	AlOOH
—	Boehmite	AlOOH

Rainwater samples collected from FT-0 had conductivity levels between 25 and 100 micromhos, sulfate values below 1 mg/L (except for two samples), and acidity values indicating neutral to only slightly acidic water. FT-1 is not included in the figures, but parameter ranges are 1,400-13,000 micromhos for conductance, 1,100-9,750 mg/L for sulfate and 132-7,487 mg/L for acidity.

Dissolved metal concentrations demonstrated the greatest fluctuations. Total Fe; Cu and Zn concentrations were generally below detection limits in the treated models. Aluminum, however, due to the low detection limits of the analytical methods used, was consistently measured in tank effluents. Manganese was also detected in most samples. Figures 28 and 29 show Al con-

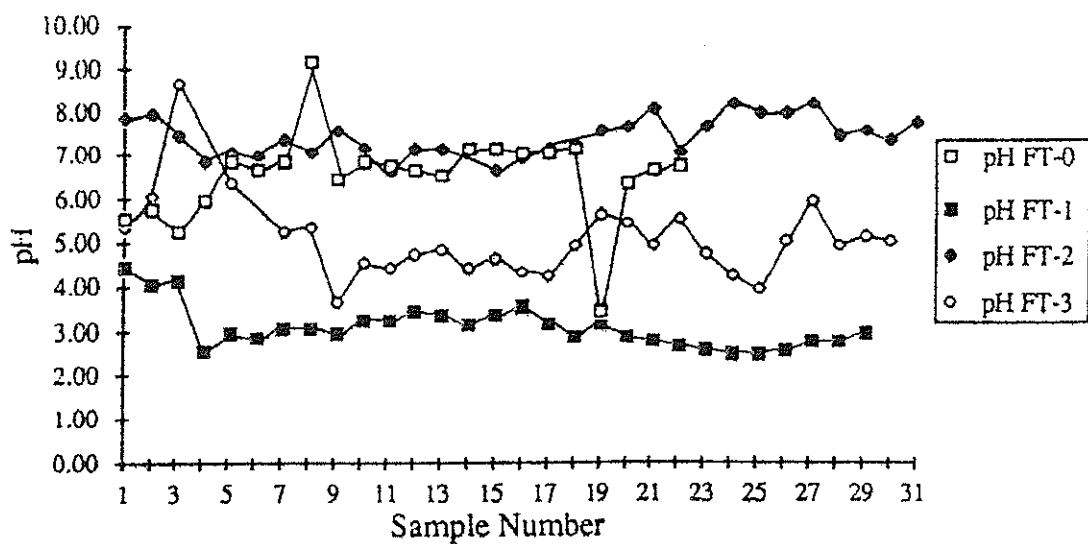


Figure 20. Plot of pH versus sample number for FT-0, FT-1, FT-2, and FT-3.

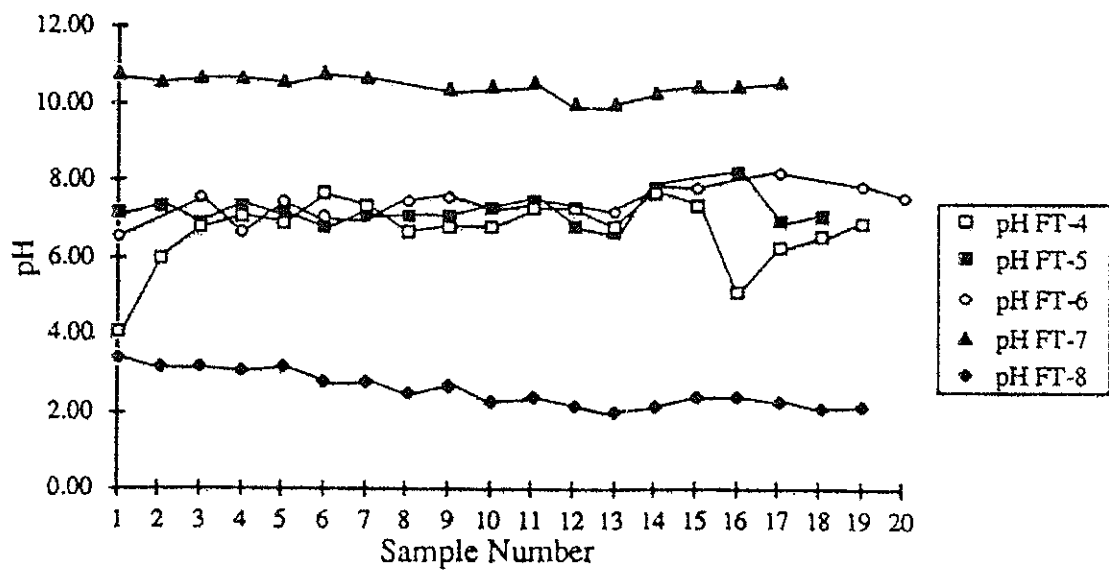


Figure 21. Plot of pH versus sample number for FT-4, FT-5, FT-6, FT-7, and FT-8.

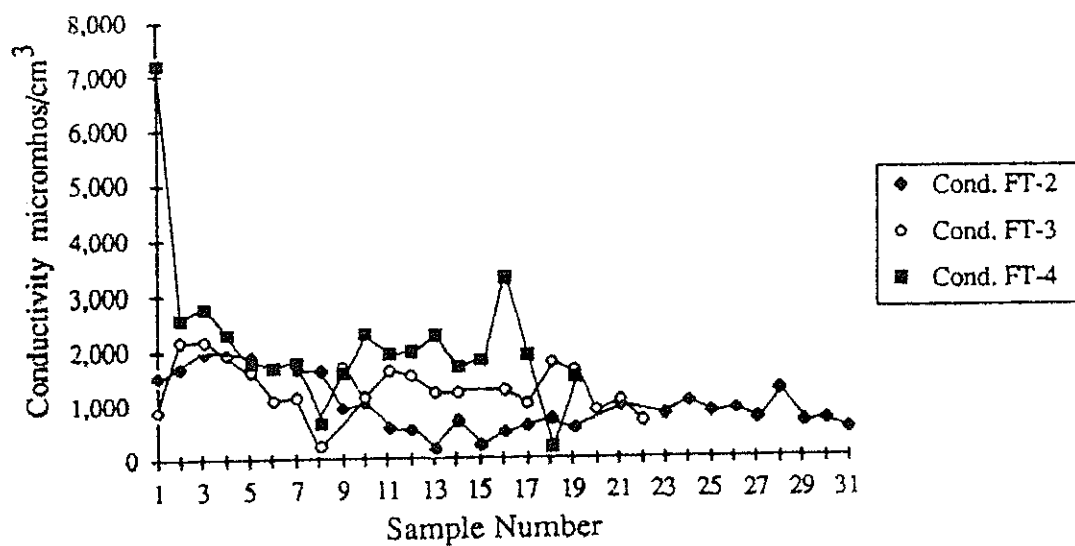


Figure 22. Plot of conductivity versus sample number for FT-2, FT-3, and FT-4.

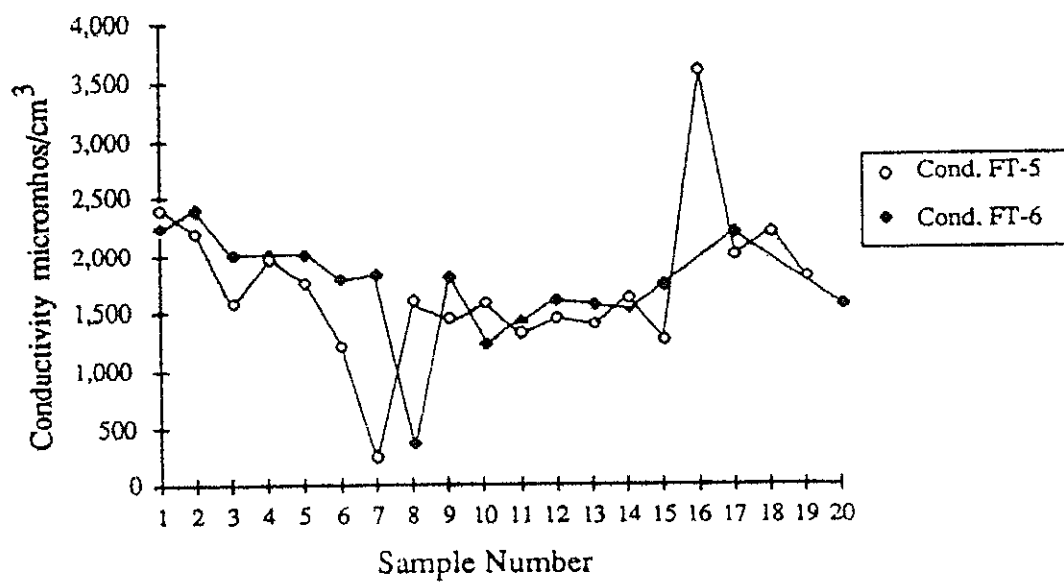


Figure 23. Plot of conductivity versus sample number for FT-5 and FT-6.

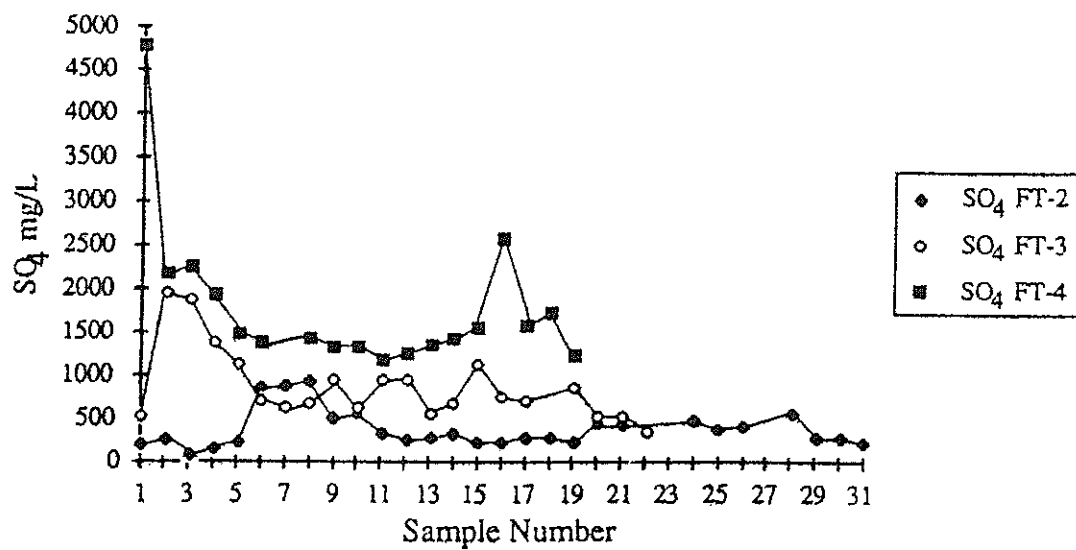


Figure 24. Plot of sulfate versus sample number for FT-2, FT-3, and FT-4.

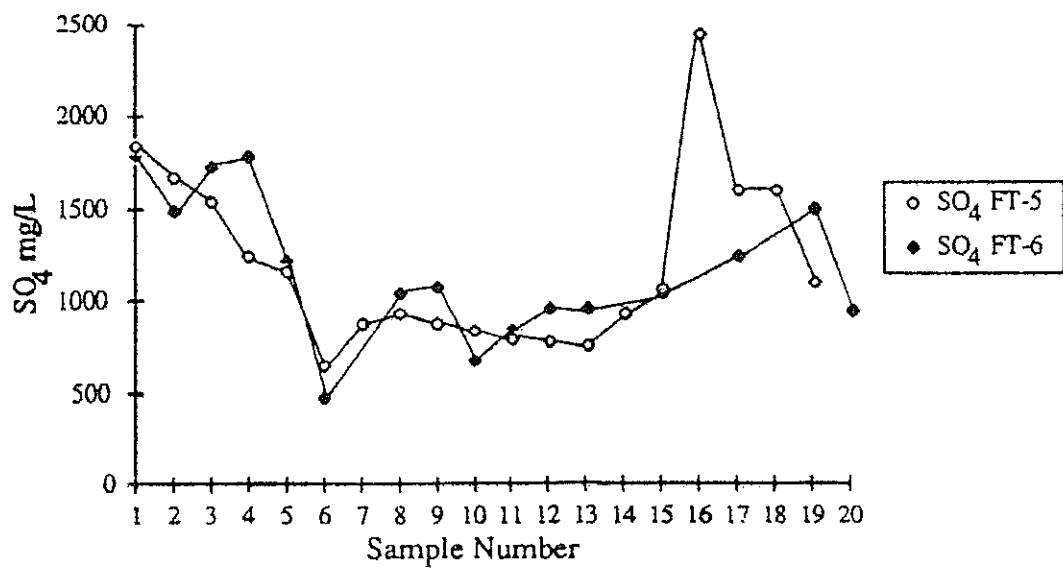


Figure 25. Plot of sulfate versus sample number for FT-5 and FT-6.

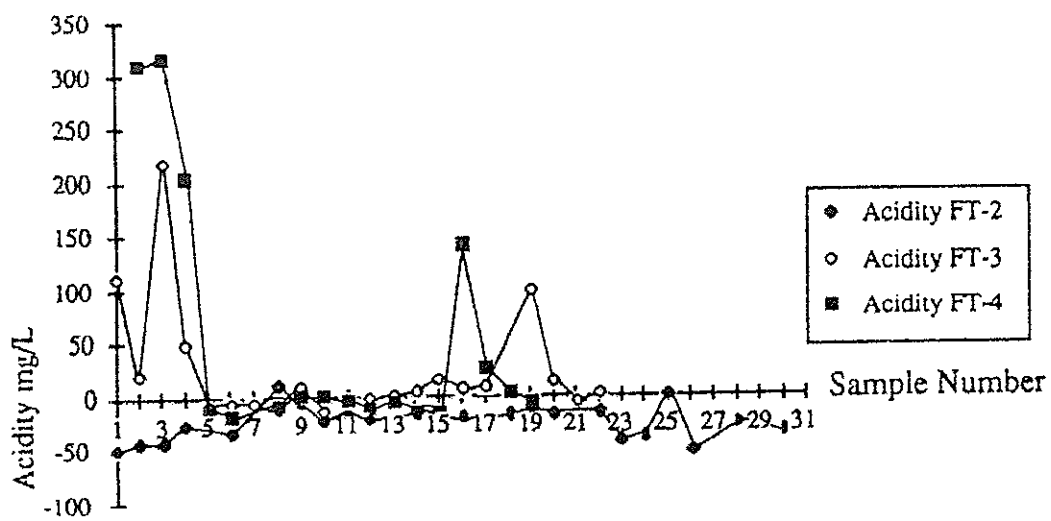


Figure 26. Plot of acidity versus sample number for FT-2, FT-3, and FT-4.

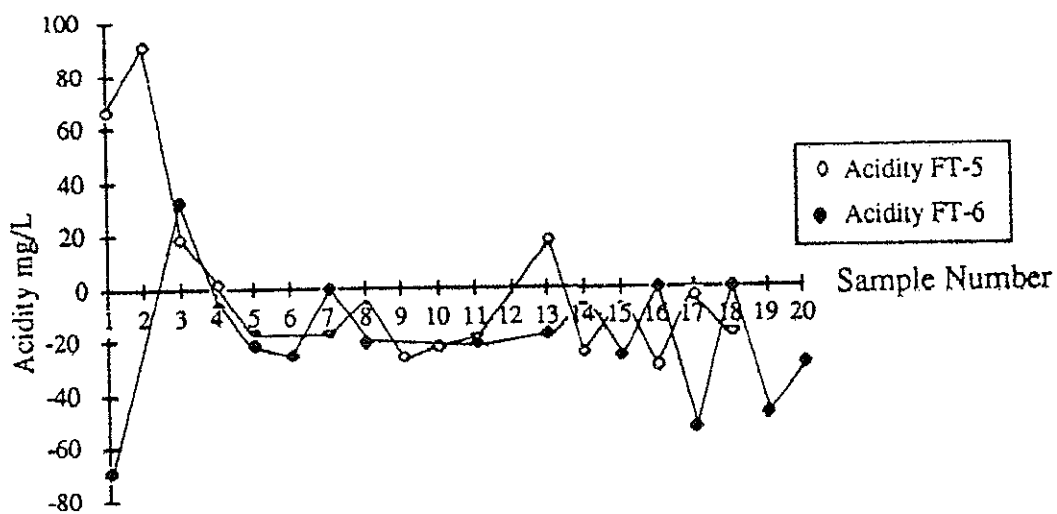


Figure 27. Plot of acidity versus sample number for FT-5 and FT-6.

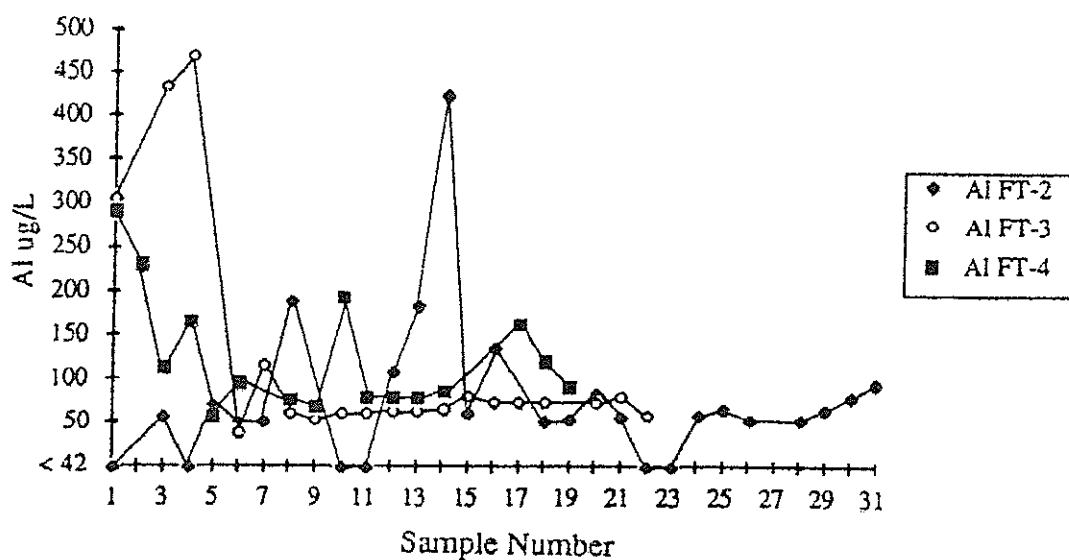


Figure 28. Plot of Aluminum versus sample number for FT-2, FT-3, and FT-4.

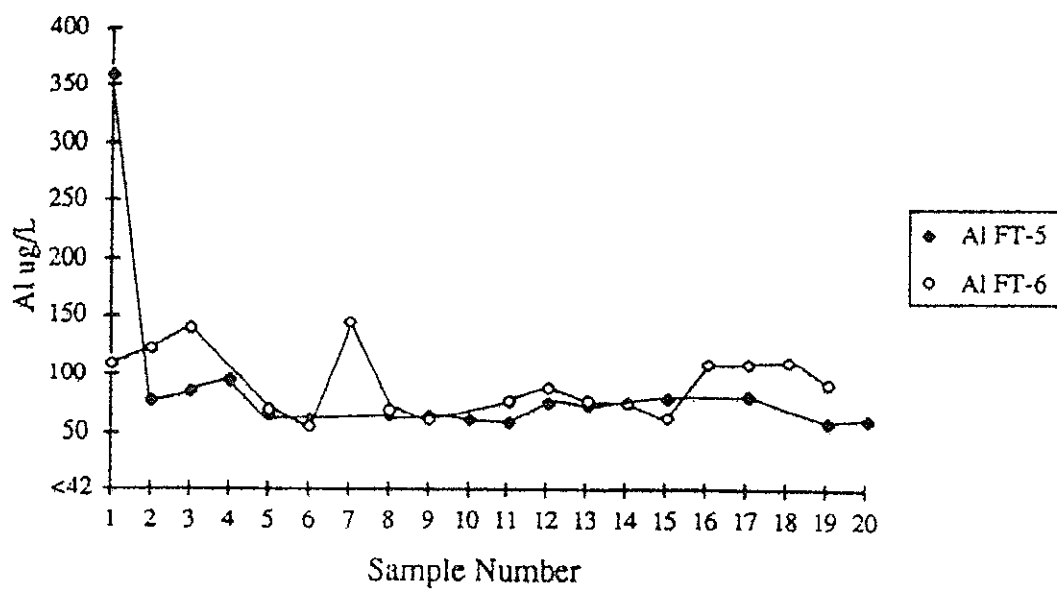


Figure 29. Plot of aluminum versus sample number for FT-5 and FT-6.

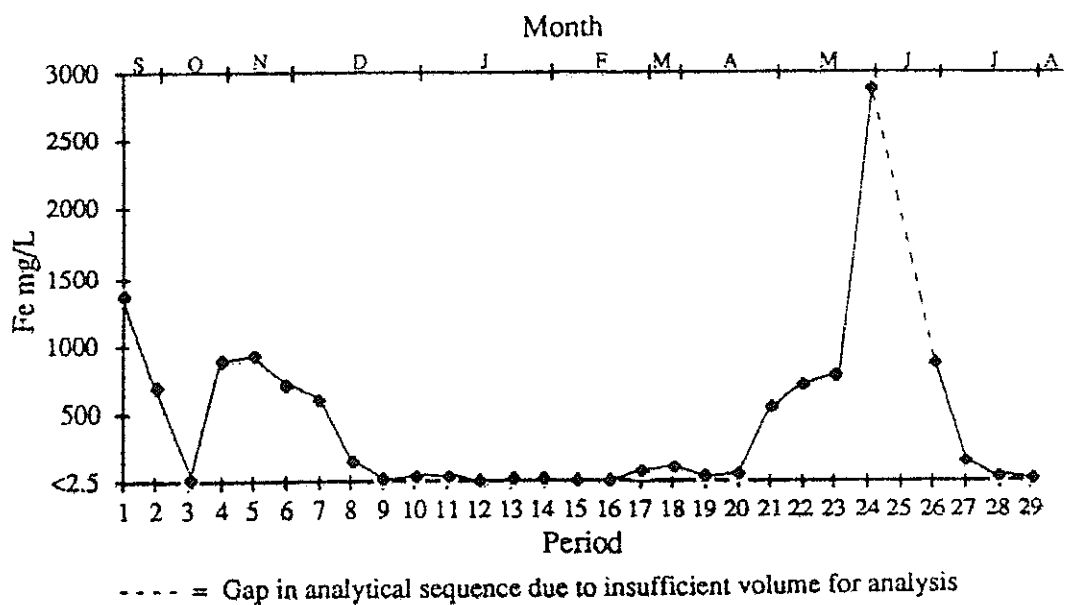


Figure 30. Plot of iron versus time for FT-1.

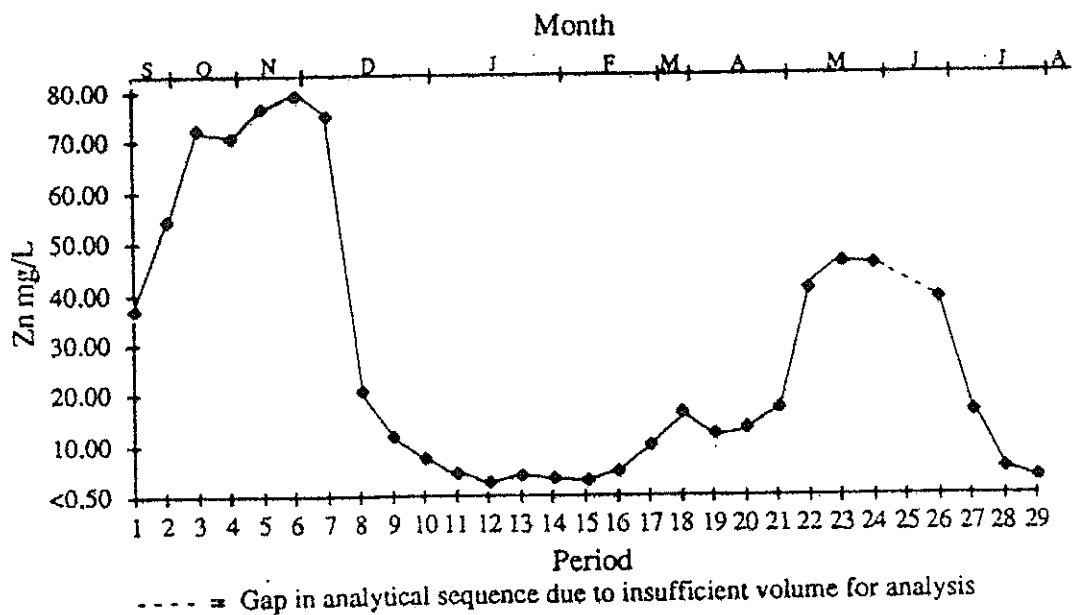


Figure 31. Plot of zinc versus time for FT-1.

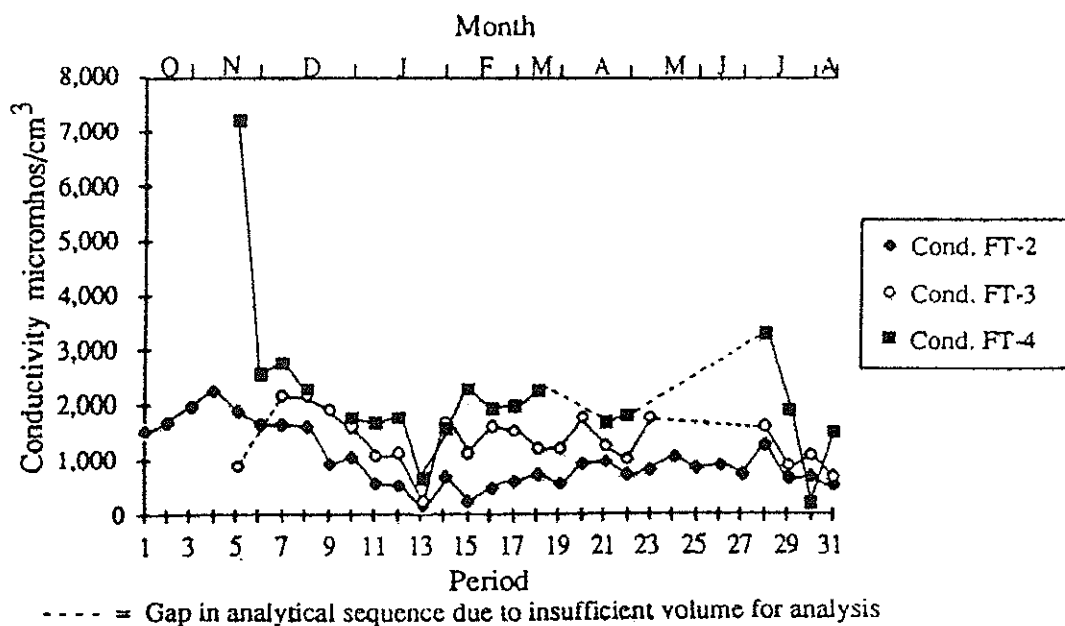


Figure 32. Plot of conductivity versus time for FT-2, FT-3, and FT-4.

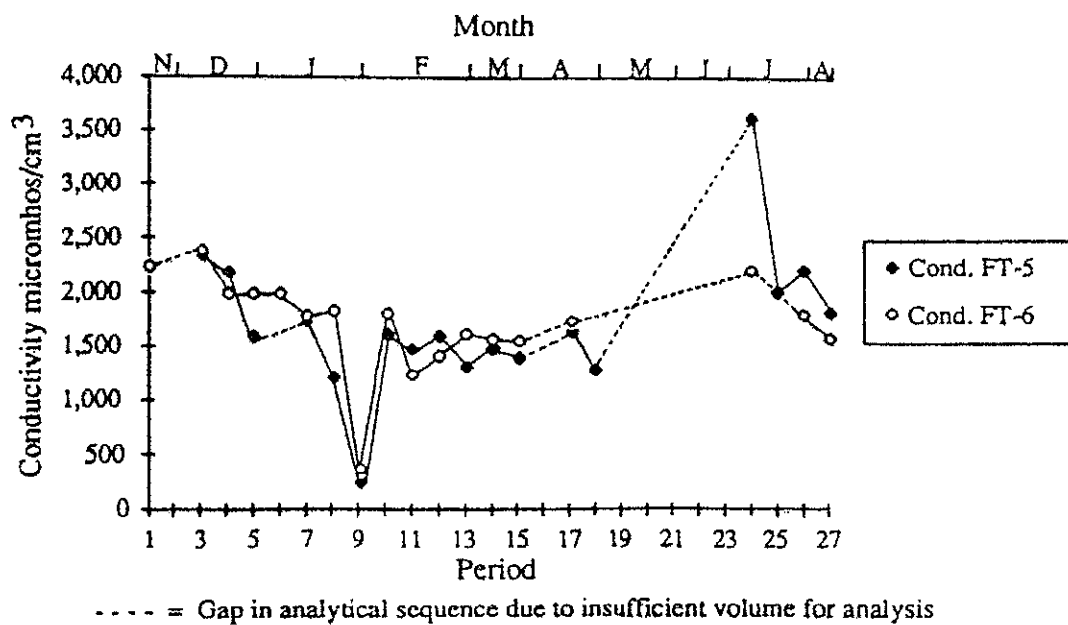


Figure 33. Plot of conductivity versus time for FT-5 and FT-6.

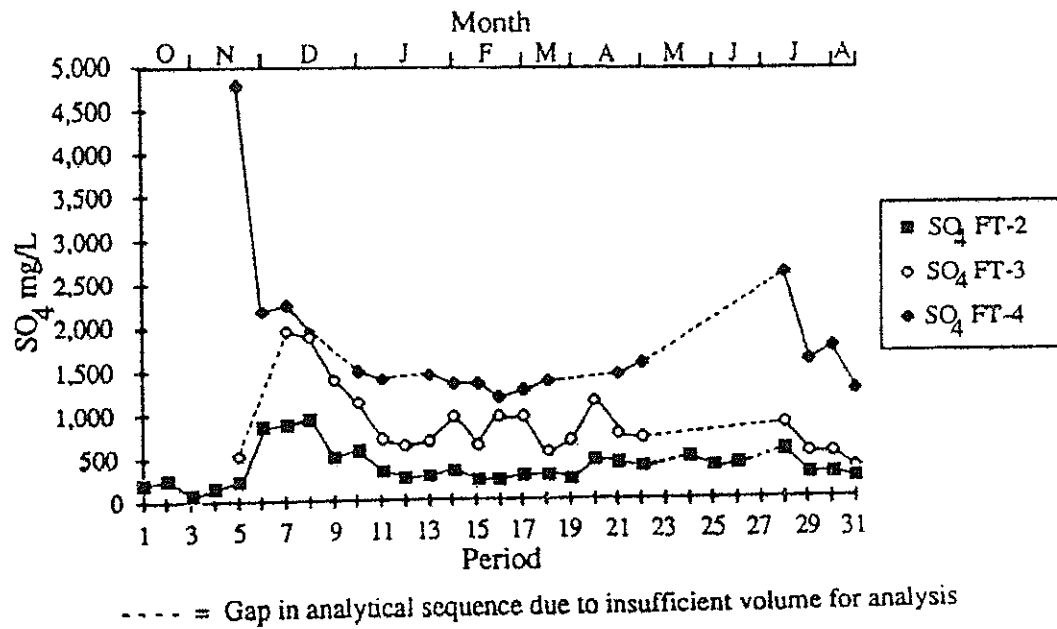


Figure 34. Plot of sulfate versus time for FT-2, FT-3, and FT-4.

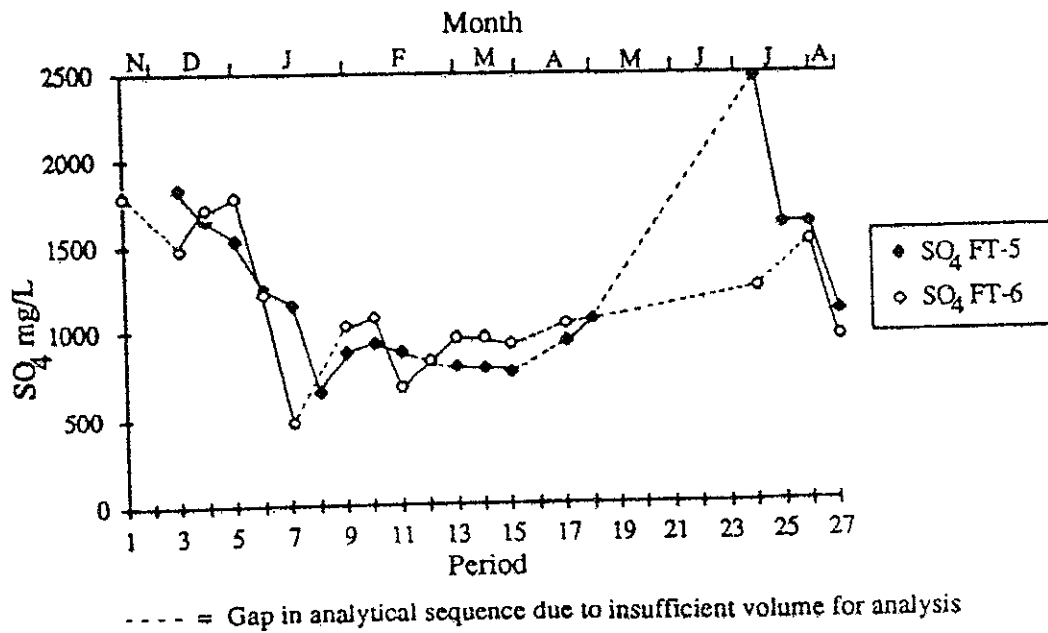


Figure 35. Plot of sulfate versus time for FT-5 and FT-6.

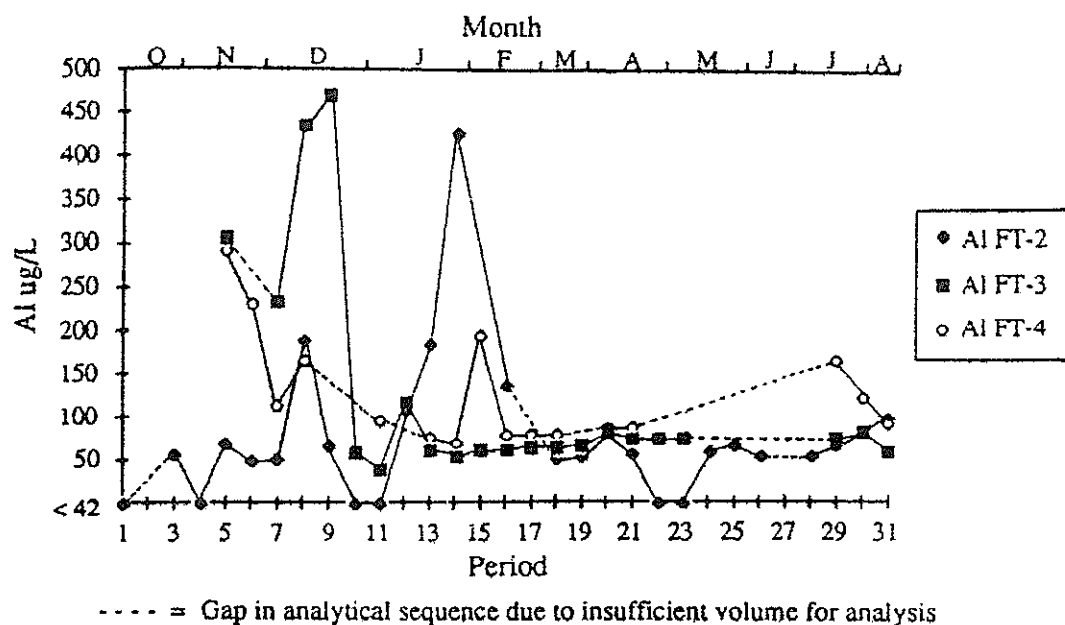


Figure 36. Plot of aluminum versus time for FT-2, FT-3, and FT-4.

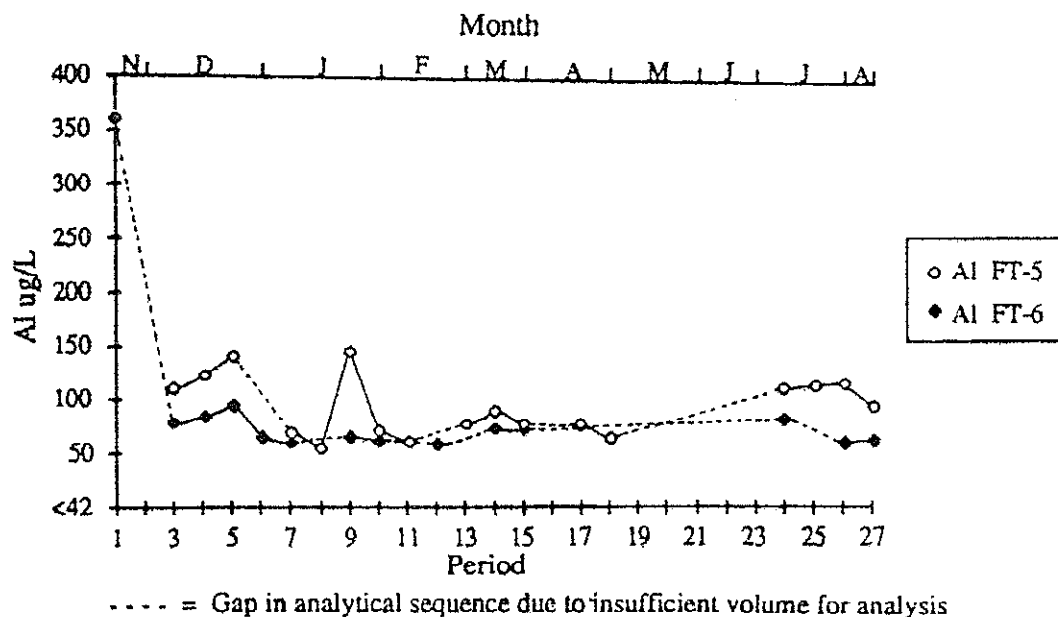


Figure 37. Plot of aluminum versus time for FT-5 and FT-6.

centrations in effluents for the treated models. Manganese values were generally in the range of 1.0 to 50.0 mg/L and exhibited trends similar to Al.

Treated models, notably FT-2, show a resistance to fluctuations in effluent quality due to variations in rainfall input and time between rainfall flushing events. Statistical comparisons of rainfall amounts between sample collection to pH, conductivity, sulfate and iron levels resulted in no correlation coefficient greater than 0.3 for any model. Therefore, rainfall amounts do not affect discharge waters to a significant degree. When the time between collection was correlated to these same four parameters in FT-1 effluents, the highest coefficient that resulted was 0.02. On this basis, the time between collection has no significant influence on water quality.

The primary influential factor affecting leachate quality seems to be seasonal variations of temperature. Figures 20 through 29 were constructed in such a manner as to show effluent quality trends for each tank from the first rainfall and flushing event. The graphs have to have an equivalent starting point specifically, the first collection from each tank, to provide a representative comparison. A representative comparison of leachate quality to rainfall input and seasonal cycles therefore, is difficult with these data plots. Figures 30 through 37 show effluent chemistry plotted against real time to illustrate seasonal patterns.

The untreated models, FT-1 and FT-8, seem to have a significant seasonal dependence on species concentrations, especially dissolved metals. Effluent quality was seen to improve slightly during the colder months when ice filled interstitial pores within the models preventing oxygen recharge and slowing sulfide oxidation rates. Leachate quality worsened considerably during warmer periods when sulfide oxidation rates and microbial activity increased. Figures 30 and 31 illustrate this trend for Fe and Zn concentrations in FT-1 leachates. FT-3, FT-4 and FT-5 effluents also seem to show a similar, but subdued, dependence on seasonal changes in temperature with respect conductivity, sulfate and aluminum (figures 32 - 37). The significant spike in conductivity and sulfate for these models, seen during July, represents a flushing event on 7-12-88 following a 60 day aeration period due to lack of significant rainfall during the months of May and June (figures 32, 33, 34 and 35). The flushing event affected metal concentrations which increased sharply. FT-6 also demonstrated increases in Mn and Zn values to above detection levels; however, these decreased to near detection levels within 17 days. In general, the treated models had much greater stability in terms of dissolved metals concentrations than models containing untreated material. Effluents from the encapsulation site underdrain (F-996) showed no seasonal variations.

Comparisons to Fill Effluents

Table 11 shows effluent quality over the time span of the study for discharge water emanating from an underdrain at the 996+50 encapsulation site (F-996-UD). These samples were analyzed to provide a baseline water quality comparison for the field models. Leachate quality from models featuring treatment by lime and limestone differs little from that of F-996-UD samples. Especially noteworthy are the small differences between FT-2, the original simulation of a fill, and actual roadfill effluent compositions. F-996-UD samples had pH ranges from 6.4 to 7.2 and an average specific conductance of 549 micromhos/cm³. Water from the fill was consistently alkaline, although it contained moderate amounts of sulfate.

Dissolved metals were consistently near or below detection levels, with the exception of manganese which averaged 2.9 mg/L. Effluents from F-996-UD showed no apparent seasonal variations. The constant quality of encapsulation site leachates over time is probably due to the insulation effects of the 6-ft (2-m) thick topsoil layer and paved highway at the upper surface. In addition, there probably is no freezing which could affect effluent quality at depth within the fill.

Field Samples

Data Trends

Surface water samples from points along

TNFLH 1-1(14) were collected when possible from 9-12-87 through 7-12-88. These samples represent water quality resulting from weathering of exposed, untreated outcrops and talus in true field settings. All of these samples were collected either from surface drainage ditches or runoff along outcrop faces. Sufficient flow for sampling usually only occurred during and shortly after a significant rainfall event. The only site which had enough flow volume for consistent sampling according to the monthly criteria was HK-SR. The remaining sites were checked on the same dates as HK-SR, but often no sample could be obtained. Table 12 summarizes the results of the field sample analyses and gives average parameter values for each of the sites. The dissolved metal concentrations had the most variability in HK-SR and C-OR with levels changing by an order of magnitude or more between sampling dates. The remaining parameters were relatively stable and demonstrated small or only moderate fluctuations. No apparent relationship resulted from comparisons of water quality at HK-SR to rainfall amounts from the 5 days prior to each collection or time between sampling. No apparent trends were observed with respect to the time of year. The quality of surface runoff obtained was probably dictated mostly by the time of sampling in relation to a specific rainfall event. If samples were collected shortly after the initiation of a storm event then runoff water would be expected to have high concentrat-

Table 11. Ranges and average values for chemical parameters in F-996-UD effluents.

Parameter	Range	Average Value
pH	6.4 - 7.2	6.8
Conductivity (umhos)	62 - 1,150	549
Sulfate (mg/L)	61 - 520	226
Acidity (mg/L)	-92 - -165	-121
Al (ug/L)	59 - 157	86
Fe (mg/L)	<2.5	<2.5
Mn (mg/L)	<1.0 - 8.4	2.9
Cu (mg/L)	<1.5	<1.5
Zn (mg/L)	<0.50	<0.50

Table 12. Average composition of surface drainage waters on TNFLH 1-1(14).

Sample N	pH	Cond.(umhos)	SO4(mg/L)	Acid.(mg/L)	Al(ug/L)	Fe	Mn	Cu	Zn .
HK-SR 6	3.3	700	227	130	5267	2.4	10.5	<1.5	0.84
A-OR 1	2.7	1875	224	701	126	ND	ND	ND	ND
A-SR 1	6.1	160	57	1	331	ND	ND	ND	ND
C-OR 2	3.0	1380	1020	990	101.6*	242.6	8.2	1.8	3.86
D-SR 2	8.4	1135	54	-114	119	<2.5	<1.0	<1.5	<0.50

N = Sample population; ND = Not determined; __* = Value is in mg/L; Fe, Mn, Cu and Zn values are in mg/L

ions of chemical species due to initial flushing or washing of oxidized material surfaces. The dilution effects of rainfall further into the event reduce species concentrations. Most surface water samples were usually collected within a day after a period of rainfall. C-OR on 12-28-87 was collected soon after the beginning of significant rainfall. Parameter values for that sample are much higher than those of any other samples which were all taken at some point after a storm.

These samples show that water quality from untreated rock exposed along these roadcuts can be highly acidic and contain toxic quantities of dissolved metals. The water quality generated along such intervals generally is that which should be expected given the acid-base accounting data characterizing these materials. Only surface water along section D, from which Comp D (NNP= -8) was obtained, proved to be of consistently better quality than expected.

Mineralogical Characterization of Encapsulation Sites

A mineralogical characterization of materials obtained from the fills by borehole was made to further evaluate the chemical environment within encapsulation sites. Three encapsulation sites on TNFLH 1-1(14) were drilled for this study using a power auger and split spoon sampler. One untreated fill (BH-1) west of this segment was augered to provide a baseline comparison. Composite samples

were obtained from a split spoon core by scraping materials at points where coatings and precipitated phases were most prevalent. The composite was ground by mortar and pestle and a packmount prepared for X-ray analysis. An identical analytical program and the same identification criteria used for X-ray analysis of laboratory composites was used for borehole samples. Binocular microscope examinations of were also conducted on uncrushed samples. Results of the mineralogical characterization are similar to data presented in table 10.

Phases present in these boreholes were similar to those found in the lab columns. Ferrihydrite was prevalent in the core material, but this was expected since pH conditions are higher within the fill than in the laboratory columns or untreated fill materials. The potassium iron sulfate, yavapaiite, was also observed in materials from two of the fills.

DISCUSSION

Lab Column Trends

Acid Production Rates

The long-term laboratory leaching tests indicate that the effluent composition from each particular column seems to be dependent on the nature of the input rock. Specifically, pH and acidity levels appear to be related to the NNP of the source. Acid production in

the lab column leachates, as indicated by these two parameters, rapidly reaches a constant level. This level was different for each of the columns. At the end of the 45 leaching cycles, acidity levels demonstrated no sign of improvement. Considering the small volume and average particle size of the composite samples, this trend suggests that the pyritic materials used in this study are capable of producing acid drainage for long periods of time. Hood and Oertel studied conductivity and Na/Ca ratios of actual field effluents from cast piles over time and estimated that each leaching cycle in their study represented approximately 3 years of natural weathering.(15) The style of comparison used in that study was not possible for the present leaching experiments since large cast piles of overburden are not exposed on TNFLH 1-1(14). However, the assumption may be made that the columns do represent an accelerated rate of acid production due to the frequency of flushing, volume of input rock and small particle size factors mentioned previously. On this basis, the leaching studies suggest that significant acid production from untreated, sulfidic Ocoee rocks may occur for at least several decades in the field. Further evidence is provided by the poor quality of surface water samples collected from the base of 10 year old roadcut exposures on TNFLH 1-1(14) and Hemlock Knob.

Theoretically, acid production from these sources should cease when the available

supply of pyrite is depleted through oxidation. The sulfur speciation study on HK-1 and HK-2 indicates that nearly all of the sulfide sulfur phases and hence, the sulfide source, was oxidized after approximately 2 years of leaching alternating with aeration. Despite the fact that pH and acidity values were still low at the end of the leaching experiments, the possibility exists that these two columns may have been close to a point where improvements in leachate quality begin to occur.

In HK-2, the initial inundation of the source material with CaCO₃-saturated water in 1986 seemed to have long-term effects on the amount of acidity produced. Despite the better effluent quality, the total amount of sulfide sulfur phases present at the end of the experiments was essentially equal to HK-1. Apparently enough residual carbonate remained in the column to buffer the leachate, but not to slow the oxidation of sulfides. In the remaining columns examined for sulfur distribution, approximately one-half of the original total sulfur percentage had been depleted after 45 weeks of leaching. These columns seem to follow a trend consistent with that of HK-1 and HK-2 and therefore, about half of the significant acid-production life of the material remained after the experiments.

Column Geochemistry and Mineralogy

When the laboratory leaching columns were initially charged, the extremely fine sulfidic material generated by the pulverization pro-

cess oxidized rapidly. The first few cycles reflected this oxidation by showing high concentrations of dissolved metals, (except Al). In addition, high sulfate, acidity, pH and conductivity levels were observed, which subsequently decreased rapidly. As the pH dropped, dissolution of primary phases other than sulfides increased. Once acidity and pH values decreased to a point where a propagation cycle was established, all parameters began to stabilize. *Thiobacillus ferrooxidans* is assumed to have catalyzed sulfide oxidation since this strain of bacteria is ubiquitous in natural materials. However, specific identification tests were not conducted to confirm bacteria presence or absence.

Once the acid production cycle was established, many geochemical changes appeared to have occurred over time. Sulfur present as sulfide phases was either redistributed as sulfate phases or was rendered into a dissolved state and exited the columns with effluents. Sulfur bound with organic materials is highly resistant to leaching and tends to remain in a system.⁽²⁾ The oxidizing environment within the columns is not conducive to the formation of any additional organically-bound sulfur; however, examination of HK-1 and HK-2 show that approximately 98 percent of the total sulfur in post-leaching materials is bound with organics. Since additional organic sulfur was probably not forming within the columns, the interpretation is that it remained the same in relation to decreases in the relative

proportions of the other two forms. The remaining columns showed that approximately 50 percent of the total post-leaching sulfur was present as sulfate phases.

Alteration and dissolution of primary phases, especially albite, seems to occur over time within the columns. In addition, micaceous minerals such as muscovite and clinochlore (chlorite) probably experience significant alteration. The dissolution of these minerals provides a source for major cations, in addition to Al, and allows the formation of secondary phases such as jarosite, yavapaiite and alunite. The high iron and sulfate concentrations further aid in the formation of jarosite seen in HK-1 and Comp C (tables 9 and 10). The probable presence of jarosite in HK-2 was unexpected since pH conditions within this column were ordinarily higher than 4.8. This phase may have formed in HK-2 in residual water left in the column after draining or directly along sulfide mineral surfaces where localized pH was probably much lower than the effluent as a whole. The presence of melanterite in HK-1 and HK-2 indicates that evaporation during the aeration stage of each leaching cycle was sufficient to allow for formation of this phase. The oxidation of melanterite during the inundation stages of each cycle would be expected to produce copiapite. Copiapite was observed in all three columns examined for the mineralogical characterization; however, melanterite was not observed in Comp C. All of the available melanterite may have been

oxidized during each recharge. The presence of ferrihydrite in HK-2 was not unexpected; yet this phase also seemed to be present in HK-1 where pH conditions were well below the ideal range for formation. Since ferrihydrite does not precipitate directly from a saturated media when pH values are less than 4.8, the source for this mineral is apparently the dissolution of copiapite and/or the decomposition of jarosite. Other phases identified in the columns include diaspore and boehmite in Comp C. These minerals are not unexpected given the relatively high Al concentrations seen in leachates from this column.

Comparisons to Field Methods and FHWA Predictive Measures

Laboratory composite B and field leaching model FT-1 incorporated untreated sulfidic material from the same source interval to establish a comparative base between lab and field leaching programs. Hood and Oertel determined that chemical species concentrations in leachates from laboratory experiments similar to those used in the present study were approximately 4.5 times less than actual mine drainage concentrations.(15) Similar general trends in chemical composition were observed between Comp B and FT-1; however, FT-1 effluents were far more concentrated. Comparisons of average conductivity, sulfate and acidity over the entire FT-1 leaching program to the same parameters, averaged over the last 5 cycles in Comp B, were done to establish

specific ratios. Conductivity in FT-1 was 11 times higher, on average, than stabilized values of the Comp B leachates. Sulfate and acidity were 24 and 32 times greater, respectively, in FT-1 effluents. Therefore, with the source materials used in this study, the longer oxidation periods and higher temperatures during warmer months generates significantly more acidic waters in the field tests than those from the laboratory columns.

Relationships of the lab results to predictive methods used by the FHWA were examined to determine the effectiveness of current evaluation procedures. Specifically, the acid-base accounting results shown in table 7 were compared to effluent quality. Good correlation appears to exist between the NNP estimates and all column leachates except Comp D. NNP values for the Hemlock Knob, Comp B and Comp C materials indicate significant potential for acid drainage. These columns, with the exception of HK-2, show highly acidic leachates. MGQ acid-base accounting indicates that alkaline, or at least neutral, water would result from contact with these rocks. The MGQ column had the best water quality of all of the leaching tests. Comp A NNP values show that the input material was only marginally deleterious, and effluent quality substantiates the estimate. Comp D NNP estimates indicate a moderate potential for acid production, yet effluents from this test were comparable to Comp A leachates. The possibility exists that discrepancies in the sampling methods used

in this study and those utilized by the FHWA resulted in the lack of correlation for Comp D. The acid-base accounting procedure used by the FHWA provides a worst-case assessment of acid production characteristics since sulfide dissolution is forced by acid digestion and all sulfur is assumed to occur as sulfide phases which have a tendency to leach easily. However, the NNP estimates are good general AD predictors when applied to sulfide-bearing, meta-sedimentary rocks in the study area.

Field Leaching Studies

Relative Effectiveness of the Model Variations

Variations in effluent quality were generally small among models featuring treated material, FT-7 excluded. Comparisons of treated to untreated effluents show that metal concentrations, with the exception of copper, are up to an order of magnitude greater in untreated leachates. FT-2, the original model, had slightly better water quality than the other tanks. The increases in conductivity, sulfate, iron and manganese in FT-4, FT-5 and FT-6 may be due to the increased volume of pyritic material incorporated into these models as compared to FT-2. FT-3 leachates improved to levels similar to the original model, although the recovery period was substantial, and acidity never attained levels commensurate with the degree of limestone addition. FT-4 seemed to have consistently higher values of conductivity and sulfate than expected, in consideration of

the 30 percent limestone reduction. This aberration may be due to higher initial sulfide concentrations in the source material. Despite precautions to avoid significant sampling variability, natural variations in sulfide mineralization, within the stratigraphic unit, make exact duplication of the large volume of rock incorporated into the models impossible.

The small differences seen in effluent chemistry from the treated field tanks indicate that water quality representative of encapsulation site effluents may be attained, despite reductions in the basal limestone aggregate layer of up to 60 percent. Topsoil reductions by 50 percent do not appear to affect the character of leachate. Placement of the buffer layer at the top of the pyritic volume was not immediately effective in improving leachate quality.

These findings suggest that the addition of interlayer lime and a basal position of the limestone aggregate layer are the influential factors in improving leachate composition. Since reductions in the thickness of limestone aggregate did not appear to seriously alter effluent chemistry, the lime treatment is probably the single most critical amendment in improving discharge waters. The addition of interlayer lime is assumed to have maintained moderately alkaline conditions within the pyritic material volume. The pH increase drives metal solubilities downward and reduces the values of acidity, sulfate and conductivity prior to interception by the limestone blanket.(20)

Concentrations of chemical species that are in a dissolved state are further decreased by the formation of oxide, hydroxide and sulfate phases in stable environments within interstices of the sulfidic mass or along the surfaces of acid-producing particles. The formation of secondary phases at these sites reduces their formation along particle-solution interfaces within the limestone blanket. This, in turn, allows the aggregate layer to remain mostly free of mineral coatings and can serve effectively to induce additional alkalinity to discharge waters. The field tanks were not dismantled to examine the nature and distribution of precipitated phases; however, visual inspection, of basal limestone aggregate obtained from the encapsulation site penetrated by BH-3, indicated no appreciable coating of the buffer material approximately 10 years post closure.

Comparisons to Baseline Water Quality

Baseline water quality data was provided by samples from a fill underdrain at station 996+50. The data trends indicate that the models featuring lime and limestone treatment provide an accurate assessment of fill leachate chemistry. Especially noteworthy are the small differences between FT-2 and F-996-UD effluent chemistry. FT-2 effluents contained only slightly higher amounts of dissolved sulfate and were slightly less alkaline. The remaining parameters show nearly identical ranges. Untreated material in FT-1 produced

leachates having average conductivity, sulfate and acidity levels which were 7, 15, and 16 times higher, respectively, than average fill discharge values. The remaining model variations, with the exception of FT-7, had pH and dissolved metal ranges comparable to F-996-UD. Stabilized values of conductivity and sulfate were approximately 3 to 10 times greater than fill effluents depending on the particular model. Acidity values for these models were comparable to FT-2 leachates, which, as previously mentioned, were 16 times greater than baseline. Despite the moderate variations in conductivity, sulfate and acidity, the FT-3, 4, 5, and 6 models produce general leachate quality comparable to encapsulation site discharges.

Fill Geochemistry and Mineralogy

The results of the bench and field scale leaching studies and mineralogical characterization of borehole materials allow some inferences to be made about chemical conditions within an encapsulation site. Mineral phases generated in the encapsulation sites by sulfide weathering are similar to those found in the lab leaching tests. The presence of secondary potassium iron sulfate minerals, such as jarosite and yavapaiite, indicates that dissolution of primary phases occurs which, in turn, supplies major cations to interstitial waters. Calcium minerals, such as gypsum, and carbonate minerals, such as calcite and

siderite, were more prevalent in the the encapsulation sites than in the lab columns due to fill lime treatment.

In untreated fill materials taken from BH-1, no unoxidized sulfides were found either by visual inspection or X-ray analysis. Material was extensively degraded and cemented by secondary phases in many places. Fresh, unaltered sulfides were identified by one or both methods in BH-2, BH-3 and BH-4.

Each length of core was tested for the presence of alkaline zones by reacting the entire length with 10 percent HCl applied by a wash bottle. This test indicates that significant alkaline zones, consistent with the frequency of lime application during construction, are still present within the encapsulation sites on TNFLH 1-1(14). Mineral precipitates and clay materials appeared to be more prevalent in these zones. Limestone underblanket samples taken from BH-3 show no significant coating of the particles.

The nature and distribution of secondary mineralization and the good effluent quality at F-996-UD indicates that the internal chemical conditions suggested for the field models also applies to the encapsulation sites. The addition of interlayer lime seems to encourage the development of alkaline conditions within the body of the fill. The increase in pH has several effects. First, *Thiobacillus ferroxidans* does not have the opportunity to catalyze sulfide oxidation. Secondly, the increased pH values lower metal solubilities and help to further

decrease species concentrations by promoting the formation of phases in interstices and along sulfidic material surfaces. Lastly, the formation of mineral phases at these sites serves to armor acid-producing particles from further oxidation, helps to reduce fill porosity and permeability, and reduces mineral phase formation along particle-solution boundaries within the limestone underblanket.

Effectiveness of Current FHWA Technology

Alkaline effluents and presence of abundant fresh sulfides in encapsulated materials demonstrates that the fill design used on TNFLH 1-1(14) is effective in retarding significant sulfide oxidation. Water quality representative of area surface streams from the encapsulation site at 996+50, approximately 10 years post closure, indicates that the current encapsulation method represents a long-term solution to AD in a highway construction setting. However, the results from the field-scale models show that significant reductions in the amount of basal limestone aggregate do not seriously degrade effluent quality. Since the field leaching tests represent accurate models of the fills, analogous reductions of limestone aggregate in the encapsulation sites may be assumed to produce similar results.

Comparisons of the laboratory leaching tests to acid-base accounting measures used by the FHWA show that the current predictive measures are adequate for assessing the

disposition of materials that are encountered during construction. This method, as used by the FHWA, may be considered as a worst-case prediction technique for reasons stated earlier.

CONCLUSIONS

Interpretation of the results of the study produced several conclusions as related to the laboratory leaching experiments. These conclusions include:

1. Differences in leachate quality among a series of laboratory leaching experiments incorporating different source materials of various lithologies indicate that the chemical composition of acidic effluents is dependent upon the mineralogical, chemical and NNP characteristics of the source material.
2. Sulfur phase distribution studies of materials from bench-scale leaching tests show that almost all sulfur bound as sulfide phases is either redistributed into sulfate phases or flushed from the system after 2 years of weekly flushing alternating with aeration. Organic sulfur appears to remain relatively constant during long-term oxidation. On this basis, the presence of substantial sulfide sources and hence, the acid-production life of sulfidic Ocoee rocks in laboratory leaching studies, such as used in this study, seems to be approximately 2 years.
3. The results of the sulfur redistribution studies, along with the fact that a previous study determined that each laboratory leaching cycle represents approximately three years of natural weathering, suggest that sulfidic Ocoee rocks are capable of significant acid production for several decades in the field.(15)
4. The oxidation of sulfides, along with leaching and hydration of other primary minerals such as albite, muscovite and chlorite, in acidic water, provides a source for species which result in abundant secondary mineral formation. Mineral phases resulting from the weathering of Ocoee rocks include jarosite, copiapite, ferrihydrite, aluminum oxides and hydroxides, and kaolinite.
5. Comparisons of average conductivity, sulfate and acidity values in laboratory leachates with the same parameters in field leaching test effluents show that the field models have values that are 11, 24 and 32 times higher respectively, than those of the lab columns. On this basis, no specific ratio provides a consistent, quantitative measure of the difference in effluent quality between laboratory and field tests.
6. FHWA acid-production predictive measures (acid-base accounting) generally have good correlation with the characteristics of effluents obtained from the leaching of similar source material. Therefore, these measures are adequate predictors of AD when applied to sulfide-bearing Ocoee

rocks in the study area.

Conclusions resulting from the field leaching tanks and encapsulation site investigation are as follows:

1. Field leaching models featuring lime and limestone treatment variations have leachate compositions similar to actual encapsulation site effluents.
2. Field-scale models featuring variations of present encapsulation techniques show that separate reductions in the quantity of the limestone aggregate layer by 60 percent and topsoil cover by 50 percent do not substantially degrade water quality.
3. A basal position of the limestone aggregate layer within a roadfill model is critical for establishing rapid recovery of effluents to acceptable quality.
4. Statistical modeling indicates that variations in rainfall amounts or length of time between flushings do not significantly affect leachate quality.
5. Seasonal temperature variations seemed to have a significant effect on field leaching test effluent quality, especially unencapsulated materials.
6. The addition of interlayer agricultural lime between layers of sulfidic material is the single most influential factor affecting leachate quality.
7. The addition of interlayer lime promotes the development of neutral conditions within the the body of a fill. These conditions allow the formation of secondary minerals to occur within the fill body rather than along particle-solution boundaries within the limestone underblanket. This, in turn, allows the limestone aggregate layer to remain uncoated and intact and can serve effectively to induce additional alkalinity to discharge waters.
8. The quality of surface water obtained from the base of sulfidic roadcuts on TNFLH 1-1(14) and Hemlock Knob indicates that these exposures continue to generate substantial AD after approximately 10 years.
9. Current FHWA encapsulation technology seems to be a long-term method to prevent AD in highway construction settings. A more economical variation, however, might include reductions in the limestone underblanket and/or amount of topsoil cover.

APPENDIX B

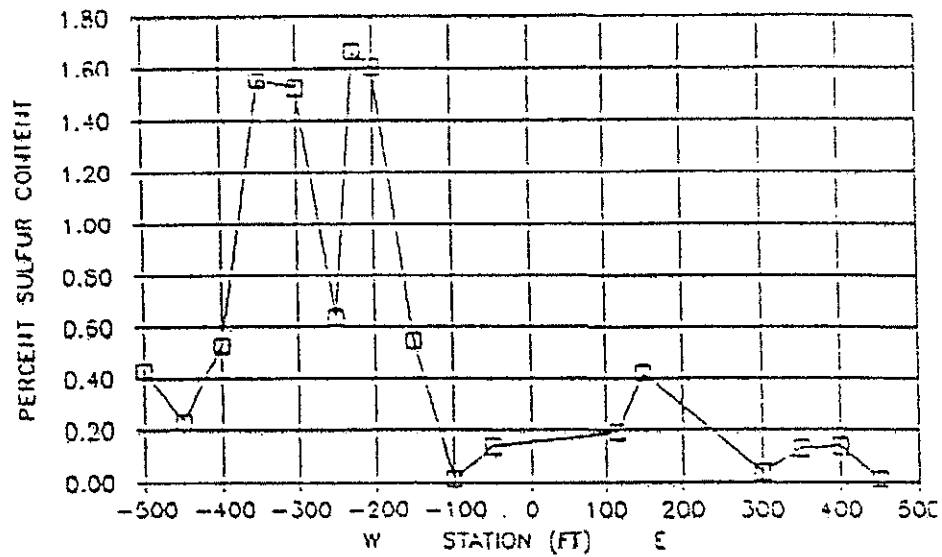
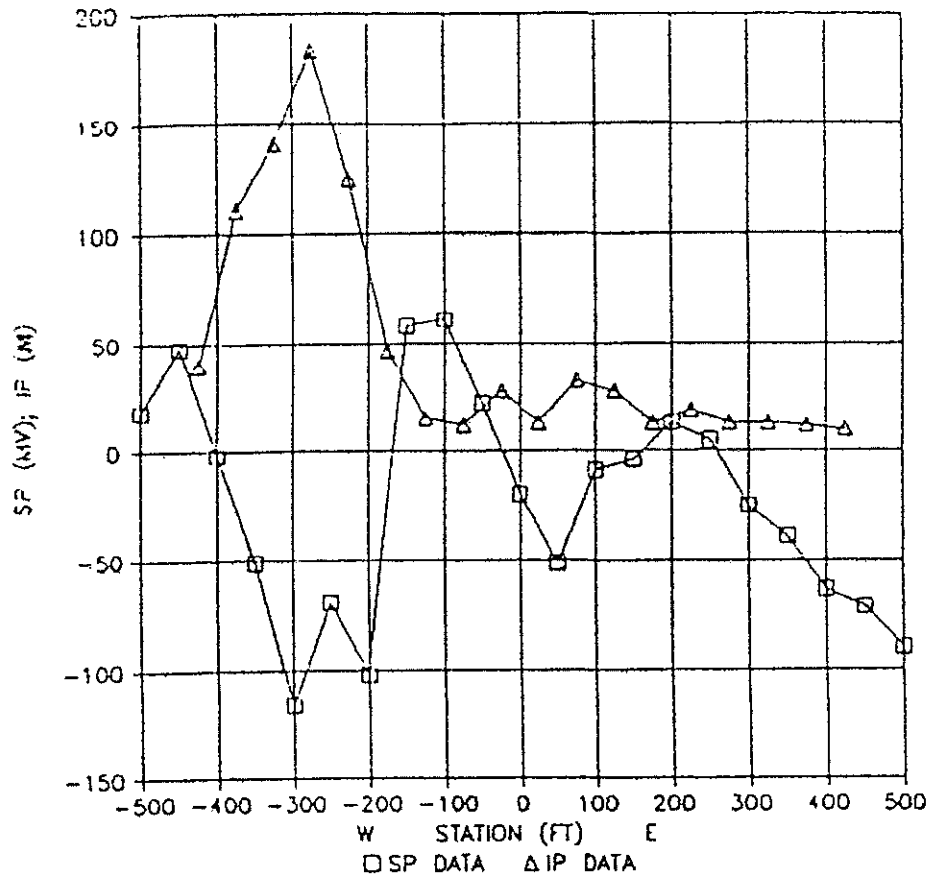


Figure 38. Correlation between geophysical data sulfide sulfur in rocks along a traverse in the Blue Ridge of Tennessee.

REFERENCES

- (1) L. Peltier, 1950, *Annals of American Geographers*, 40:219, fig. 3.
- (2) A.A. Sobek, W.A. Schuller, J.R. Freeman, and R.M. Smith, 1978, *Field and Laboratory Methods Applicable to Overburdens and Minesoils*: U.S. Environmental Protection Agency, Pub. No. EPA-600/2-78-054, 204 p.
- (3) D.H. Jones, B.S. Bell, and J.H. Hansen, 1981, The application of induced polarization in highway planning, location, and design: *Proceedings, 32nd Annual Highway Geology Symposium and Field Trip*, Gatlinburg, Tennessee, pp.154-173.
- (4) M. Sato and H.M. Mooney, 1960, The electrochemical mechanism of sulfide self-potentials: *Geophysics*, Volume 25, No. 1, pp. 226-249.
- (5) P.M. Erickson and K.J. Ladwig, 1986, Field observation of potential acid sources within surface mine backfills, *Proceeding , Seventh West Virginia Surface Mine Drainage Task Force Symposium*, Morgantown, WV.
- (6) A.E. Whitehouse and J.R. Straughan, 1986, Ammonia - the rest of the story: *Proceedings, Seventh Annual West Virginia Surface Mine Drainage Task Force Symposium*, Morgantown, West Virginia.
- (7) P.C. Singer and W. Stumm, 1970, Acid Mine Drainage: The Rate Determining Step: *Science*, Vol. 167, February, pp. 1121-1123.
- (8) D.K. Nordstrom, 1982, Aqueous Pyrite Oxidation and the Consequent Formation of Secondary Iron Minerals: in: *Acid Sulfate Weathering*, Soil Science Society of America Special Publication No. 10, pp. 37-63.
- (9) J.D. Hem and W.H. Cropper, 1962, Survey of Ferrous-Ferric Chemical Equilibria and Redox Potentials: U.S.G/S. Water Supply Paper 1459-A, 73 p.

- (10) R.L.P. Kleinmann, D.A. Crerar, and R.R. Pacelli, 1981, Biogeochemistry of Acid Mine Drainage and a Method to Control Acid Formation: Mining Engineering, Vol. 33, No. 3, pp. 300-305.
- (11) H.L. Barnes and S.B. Romberger, 1968, Chemical Aspects of Acid Mine Drainage: Journal of the Water Pollution Control Federation, Vol. 40, No. 3, Part 1, pp. 371-384.
- (12) F.T. Caruccio, 1984, The Nature, Occurrence and Prediction of Acid Mine Drainage from Coal Strip Mines, Study Guide, National Symposium on Surface Mining, Hydrology Sedimentology and Reclamation, 39 p.
- (13) D.T. Rickard, 1970, The Origin of Framboids: Lithos, Vol. 3, pp. 269-293.
- (14) D.K. Nordstrom, 1985, The Rate of Ferrous Iron Oxidation in a Stream Receiving Acid Mine Effluent: U.S. Geological Survey Water Supply Paper No. 2270, pp. 113-119.
- (15) W.C. Hood and A.O. Oertel, 1984, A Leaching Column Method for Predicting Effluent Quality from Surface Mines: National Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation, Lexington, Ky., Dec. 2-7, pp. 271-277.
- (16) W.K. Dougan and A.L. Wilson, 1974, The Absorptiometric Determination of Aluminum in Water. A Comparison of some Chromogenic Reagents and the Development of an Improved Method: Analyst, Vol. 99, July, pp. 413-430.
- (17) B.R. Culver, 1975, Analytical Methods for Carbon Rod Analyzers: Varian Techtron Pty., Ltd., Springdale, Australia, Varian Associates, Palo Alto, California, Publication No. 85-1000044-00.
- (18) APHA, AWWA, ABJPCF, 1985, Standard Methods for the Examination of Water and Wastewater: 16th ed., Washington D.C., 1268 p.
- (19) Varian Techtron Pty., Ltd., 1979, Analytical Methods for Flame Spectroscopy: Varian Techtron Pty., Ltd., Australia, Publication No. 85-100009-00, 123 p.

- (20) R.C. Wilmoth, 1977, Limestone and Lime Neutralization of Ferrous Iron Acid Mine Drainage: Environmental protection technology Series, EPA-600/2-77-101, 105 p.

BIBLIOGRAPHY

W.C. Anderson and M.P. Youngstrom, 1976, Coal Pile Leachate Quantity and Quality Characteristics: Sixth Symposium on Coal Mine Drainage Research, Oct. 19-21, Louisville, Ky. , pp. 17-33.

W.M. Aston, 1974, Fool's Gold Pollutes: Canadian Mining Journal, Vol. 95, No. 3, pp.59-61.

T. Biegler and D.A. Swift, 1979, Anodic Behavior of Pyrite in Acid Solutions: Electrochimica Acta, Vol. 24, pp.415-420.

R.A. Brant, P.R. Dugan, C.I. Randles, K.S. Shumate, and E.E. Smith, 1971, Acid mine drainage formation and abatement. The Ohio State University Research Foundation. Publ. No. 14010 FPR. U.S. Environmental Protection Agency, Washington, D.C.

E. Brown, M.W. Skovgaard, and M.J. Fishman, 1970, Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases: in Techniques of Water-Resources Investigations of the United States Geological Survey, Book 5, Chapter A1, 160 p.

D.W. Byerly, 1986, Handling Excavated Acid-Producing Material: FHWA Project Proposal, 11 p.

D.W. Byerly, 1980, Environmental Geologic Studies along the Route of the Tellico Plains - Robbinsville Scenic Highway, Interim Report, U.S.D.O.T., FHWA, Region 15, Demonstration Projects Division.

F.T. Caruccio, 1969, Characterization of Strip Mine Drainage: Ecology of Drastically Disturbed Sites, Vol. 1, Gordon & Breach, Sci. Publ., Inc., pp.193-224. [AGVET S621.5.S8N37]

F.T. Caruccio, 1970, The Quantification of Reactive Pyrite by Grain Size Distribution: Proceedings of the Third Symposium on Coal Mine Drainage Research, May, pp.123-131.

F.T. Caruccio, 1973, Characterization of Strip-Mine Drainage by Pyrite Grain Size and Chemical Quality of Existing Groundwater: Ecology and Reclamation of Devastated Land, Vol. 1, Davis, G., ed., Gordon & Breach, Sci. Publ., Inc., pp. 193-226. [AGVET S621.5.S8N37]

F.T. Caruccio, G. Geidel, and J.M. Sewell, 1976, The Character of Drainage as a Function of the Occurrence of Framboidal Pyrite and Groundwater Quality in Eastern Kentucky: Sixth Symposium on Coal Mine Drainage Research, Oct. 19-21, Louisville, Ky., pp. 1-16.

F.T. Caruccio and G. Geidel, 1981, Estimating the Minimum Acid Load that can be Expected from a Coal Strip Mine, Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation, Lexington, Ky., Dec. 7-11, pp. 117-122.

F.T. Caruccio and G. Geidel, 1983, The effect of plastic liner on acid loads/DLM site, WV., Proceedings, Fourth West Virginia Surface Mine Drainage Task Force Symposium. Clarksville, WV.

F.T. Caruccio and G. Geidel, 1984, Induced Alkaline Recharge Zones to Mitigate Acidic Seeps: National Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation, Lexington, Ky., December 2-7, pp.43-47.

G.C. Claytor, 1978, An Evaluation of Geochemical Parameters of the Overburden and the Water Quality Associated with Strip Mining of the Sewanee Seam in the Southern Coal Field of East Tennessee: M.S. Thesis, Univ. of Tenn., 111 p.

J.T.Cline and R. Balla, 1976, Water Quality Relationships as a Function of AMD Inputs into the Susquehanna River: Sixth Symposium on Coal Mine Drainage Research, Oct. 19-21, Louisville, Ky., pp. 34-49.

W.R. Curtis, K.L. Dyer, and G.P. Williams, Jr., 1987, A Manual for Training Reclamation Inspectors in the Fundamentals of Hydrology, U.S.D.A., U.S.F.S., 56 p.

M.T. Dougherty and N.J. Barsotti, 1972, Structural Damage and Potentially Expansive Sulfide Minerals, Bull. of the Assoc. of Engr. Geologists, Vol. IX, No. 2, pp.105-125.

P. Eger, K. Lapakko, and P.G. Chamberlain, 1984, Mixed Disposal of Waste Rock and Tailings to Reduce Trace Metal Release from Waste Rock: Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation, Lexington, Ky., Dec. 2-7, pp. 49-56.

P.M. Erickson, 1985, Oxygen content of unsaturated coal mine waste, In: Control of acid mine drainage, Bureau of Mines Information Circular 9027, USDI, Bureau of Mines, Pittsburgh, PA, pp. 19-24.

P.M. Erickson, R.W.Hammock, and R.L.P. Kleinmann, , 1985, Prediction of acid drainage potential in advance of mining, In: Control of acid drainage, Bureau of Mines Information Circular 9027, USDI, Bureau of Mines, Pittsburgh, PA.

P.M. Erickson and K.J. Ladwig, 1985, Chemical inhibition of acid drainage formation, Proceedings, Sixth West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, WV.

E.J. Fasiska, H. Wagenblast, and M.T. Dougherty, 1974, The Oxidation Mechanism of Sulfide Minerals: Bull. of the Assoc. of Engr. Geologists, Vol. IX, No. 1, pp.75-82.

Federal Water Pollution Control Federation (FWPCF), 1970, Studies on Limestone Treatment of AMD: Water Pollution Control Research Series, Report No. 14010 EIZ 01/70, 96 p.

Federal Water Pollution Control Federation (FWPCF), 1971, Studies on Limestone Treatment of AMD Part II: Water Pollution Control Research Series, Report No. 14010 EIZ 12/71, 140 p.

K.D. Ferguson and P.M. Erickson, 1987, Will it Generate AMD? An Overview of Methods to Predict Acid Mine Drainage: in: Acid Mine Drainage Workshop Proceedings, Halifax, Nova Scotia, Mar., pp.215-244.

D. Fredley, 1981, Geology and Mineral Resources of the Cherokee National Forest, U.S.G.S., 23 p.

G. Geidel and F.T. Carrucio, 1981, The Effect of a Surface Application of Dolomite on Acidic Ground Water: G.S.A. Abstracts with Programs, Vol. 3, No. 7, p. 457.

G. Geidel and F.T. Caruccio, 1982, Acid Drainage Response to Surface Limestone Layers: Proceedings of the National Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation, Lexington, Ky., pp.5-10.

J.B. Hadley and R. Goldsmith, 1963, Geology of the Eastern Great Smoky Mountains North Carolina and Tennessee: U.S.G.S. Professional Paper 349-B, 118 p.

J.D. Hem, 1970, Study and Interpretation of the Chemical Characteristics of Natural Water: U.S.G.S. Water Supply, No. 1473, 273 p.

N.C. Hester, 1984, Sedimentary Environmental Control of Sulfur in Overburden of Coals in Eastern Kentucky: G.S.A. Abstracts with Programs, Vol. 9, No. 5, pp. 604-605.

W.H. Huang and W.D. Keller, 1972, Geochemical Mechanics for the Dissolution, Transport, and Deposition of Aluminum in the Zone of Weathering: Clays and Clay Minerals, Vol. 20, pp.69-74.

J.W. Huckabee, C.P. Goodyear, and R.D. Jones, 1975, Acid Rock in the Great Smokies: Unanticipated impact on Aquatic Biota of Road Construction in Regions of Sulfide Mineralization: Transactions of the American Fish Society, No. 4, pp.677-684.

V.J. Hurst and J.S. Schlee, 1962, Field Excursion: Ocoee Metasediments North Central Georgia-Southeast Tennessee, G.S.A. Guidebook No. 3, 28 p.

A.G. Kim, B.S. Heisey, and R.L.P. Kleinmann, 1982, Acid Mine Drainage: Control and Abatement Research: U.S. Bureau of Mines Inf. Circular, No. 8905, 22 p.

P.B. King, 1964, Geology of the Central Great Smoky Mountains Tennessee: U.S.G.S. Professional 349-C, 148 p.

R.P.L. Kleinman and P.M. Erickson, 1983, Control of Acid Mine Drainage from Coal Refuse Using Anionic Surfactants: U.S. Bureau of Mines Report of Investigations No. 8847, 16 p.

R.P.L. Kleinman, 1985, Treatment of Acid Mine Water by Wetlands: in : Control of Acid Mine Drainage: Proceedings of a Technology Transfer Seminar, U.S. Bureau of Mines Information Circular 9027, pp. 48-52.

R.A. Knapp, 1987, The Biogeochemistry of Acid Generation in Sulphide Tailings and Waste Rock: in: Acid Mine Drainage Workshop Proceedings, Halifax, Nova Scotia, March, pp.47-65.

K.J. Ladwig, P.M. Erickson, and R.L.P. Kleinman, 1985, Alkaline Injection: An Overview of Recent Work: in: Control of Acid Mine Drainage: Proceedings of a Technology Transfer Seminar, U.S. Bureau of Mines, Information Circular 9027, pp. 35-40.

D. Langmuir and M.W. Gang, 1974, Controls on Heavy Metals in some Streams and Groundwaters Affected by Coal Mine Drainage in Western Pennsylvania: G.S.A. Abstracts with Programs, Vol. 6, No. 7, pp.837-838.

K. Lapakko, 1987, Prediction of Acid Mine Drainage from Duluth Complex Mining Wastes in Northeastern Minnesota, U.S.A.: in: Acid Mine Drainage Workshop Proceedings, Halifax, Nova Scotia, March, pp.287-320.

K. Lapakko and P. Eger, 1981, Trace Metal Removal from Mining Stockpile Runoff using Peat, Woodchips, Tailings, Till, and Zeolite: Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation, Lexington, Ky., pp.105-116.

F.G. Lesure, et. al., 1977, Mineral Resources of the Joyce Kilmer-Slickrock Wilderness, North Carolina -Tennessee: U.S.G.S. Bull. 1416, 89 p.

H.W. Martin and W.R. Mills, Jr., 1976, Water Pollution Caused by Inactive Ore and Mineral Mines, A National Assessment: U.S.E.P.A.-600/2-76-296, 185 p.

MARRICH, INC., 1989, Geophysical test survey results, U.S. Highway 64 proposed relocation study, Polk County, Tennessee: Report presented to Engineering, Design and Geosciences Group, Inc., 30 p.

R.C. Mathews and E.L. Morgan, 1982, Toxicity of Anakeesta Formation Leachates to Shovel-Nosed Salamander, Great Smoky Mountains National Park: *Journal of Environmental Quality*, Vol. 11, No. 1, pp.102-106.

R.C. Mathews, J.D. Sinks, and E.L. Morgan, 1976, Acid Drainage Toxicity and Assessment of Sodium Hydroxide Neutralization in Streams of the Great Smoky Mountains: *Proceedings of the First Conference on Scientific Research in the National Parks*, Nov. 9-12, New Orleans, pp.559-564.

R.G.L. McCready, 1987, A Review of the Physical, Chemical and Biological Measures to Prevent Acid Mine Drainage: An Application to the Pyritic Halifax Shales: *in: Acid Mine Drainage Workshop Proceedings*, Halifax, Nova Scotia, March, pp. 333-356.

M.A. McKibben and H.L. Barnes, 1986, Oxidation of Pyrite in Low Temperature Acidic Solutions; Rate Laws and Surface Textures: *Geochimica et Cosmochimica Acta*, Vol. 50, No. 7, pp.1509-1520.

D. McKinney and D. Melgaard, 1979, Biological and Chemical Investigation of Selected Waters within the Cherokee National Forest, Tellico Wildlife Management Area, Monroe County, Tennessee: *Tennessee Division of Water Quality Control*, 52 p.

C.E. Merschat and L.T.Larson, 1972, Disseminated Sulfides in Late Precambrian Ocoee Rocks: *G.S.A. Abstracts with Programs, Southeastern Section Meeting*, pp.92-93.

E.W. Murray, S.P. Goudey, R.L.G. McCready, and J. Salley, 1988, Laboratory and Field Testing of a Salt-Supplemented Clay Cap as an Impermeable Seal Over Pyritic Slates: *U.S. Bureau of Mines, Information Circular 9027*, pp.52-58.

K. Nakamura, 1988, Biological Metal Removal from Mine Drainage: *in: Mine Drainage and Surface Mine Reclamation*, U.S. Bureau of Mines, *Information Circular 9183*, Vol. 1, pp. 274-278.

J.W. Nebgen, W.H. Engelmann, and D.F. Weatherman, 1981, Inhibition of Acid Mine Drainage Formation: The Role of Insoluble Iron Compounds: *Journal of Environmental Sciences*, Vol. 24, No. 3, pp.23-27.

D.K. Nordstrom, E.A. Jenne, and J.W. Ball, 1979, Redox Equilibria of Iron in Acid Mine Waters: in: E.A. Jenne, ed., Chemical Modeling in Aqueous Systems, American Chemical Society, pp.51-79.

M. O'Hagan, 1986, Admixing Limestone with Rocks Having Low, Medium, and High Sulfur Content to Mitigate Acid Mine Drainage: M.S. Thesis, Univ. of South Carolina, Department of Geology, 95 p.

H. Olem, T.L. Bell, and J.J. Longaker, 1982, Prevention of Acid Drainage from Stored Coal: Journal of Energy Engineering, Vol. 109, No. 2, June, pp.103-112.

R.M. Schuller, et.al., 1981, Evaluation of Laboratory-Produced Leachates Used for Environmental Assessment of Coal Refuse, National Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation, Lexington, Ky., pp.123-128.

M.A. Shellhorn and V. Rastogi, 1984, Laboratory Methods for Determining the Effects of Bactericides on Acid Mine Drainage: National Symposium on Surface Mining, Hydrology, Sedimentology, and Reclamation, Lexington, Ky., pp. 77-82.

P. Singer and W. Stumm, 1968, Kinetics of the Oxidation of Ferrous Iron: Proceedings of the Second Symposium on Coal Mine Drainage Research, May, pp.12-34.

J.G. Skousen, J.C. Sencindiver, and R.M. Smith, 1987, A Review of Procedures for Surface Mining and Reclamation in Areas with Acid-Producing Materials: West Virginia University Energy and Water Research Center, Publication EWRC871, 39 p.

J.F. Slack, E.R. Force, P.T. Behum, 1979, Mineral Resources of the Citico Creek Wilderness Study Area, Monroe County, Tennessee: U.S.G.S. Open File Report 79-231, 33 p.

J.F. Slack, G.C. Gazdik, and M.L. Dunn, Jr., 1979, Mineral resources of the Big frog Wilderness Study Area, Polk County, Tennessee and Franklin County, Georgia: U.S.G.S. Open File Report 79-1209, 39 p.

E.E. Smith and K.S. Schumate, 1970, Sulfide to Sulfate Reaction Mechanism: Water Pollution Control Research Series, No. 14010-FPS-02/70.

W. Stumm and J.J. Morgan, 1981, Aquatic Geochemistry: John Wiley & Sons, New York, 780 p.

P.J. Sullivan, S.V. Mattigod, and A.A. Sobek, 1986, Dissolution of Iron Sulfates from Pyritic Coal Waste: Environmental Science & Technology, Vol. 20, No. 10, pp.1013-1016.

S.G. Unger and D.L. Jordening, 1974, Bibliography of Water Pollution Control Benefits and Costs: U.S.E.P.A. Socioeconomic Environmental Studies Series, EPA-600/5-74-028, 195 p.

United States Bureau of Mines, 1985, Control of Acid Mine Drainage, Proceedings of a Technology Transfer Seminar: U.S. Bureau of Mines Inf. Circular, No.9207, 61 p.

United States Environmental Protection Agency, 1971, Silicate Treatment for Acid Mine Drainage: Water Pollution Control Research Series, 14010-DLI-02/71, 94 p.

United States Environmental Protection Agency, 1971, Studies on Limestone Treatment of Acid Mine Drainage Part 2: Water Pollution Control Research Series, 14010-EIZ-12/71, 140 p.

United States Environmental Protection Agency, 1971, Methods for Chemical Analysis of Water and Wastes: EPA-16020-07/71, 312 p.

United States Environmental Protection Agency, 1971, Inorganic Sulfur Oxidation by Iron Oxidizing Bacteria: Water Pollution Control Research Series, No. 14010-DAY-06/71.

United States Environmental Protection Agency, 1970, Treatment of Acid Mine Drainage: Water Pollution Control Research Series, 14010-DEE-12/71.

United States Environmental Protection Agency, 1970, Studies on Limestone Treatment of Acid Mine Drainage, Part 1: Water Pollution Control Research Series, 14010-EIZ-01/70, 96 p.

United States Geological Survey, 1977, National Handbook of Recommended Methods for Water Data Acquisition:

United States Geological Survey, 1962, Chemistry of Iron in Natural Water: U.S.G.S. Water Supply Paper, No. 1459, 268 p.

Water Resources Scientific Information Center, 1975, Acid Mine Water: A Bibliography: WRSIC Pub. No. 75-202, Office of Water Resources Research, Washington, D.C., 564 p.

S.A. Zaburunov, 1987, Helping Nature Help Itself: Coal Mining, May, pp.42-43.